

D E C L A R A T I O N

I, SHINICHI USUI, a Japanese Patent Attorney registered No.9694, of Okabe International Patent Office at No. 602, Fuji Bldg., 2-3, Marunouchi 3-chome, Chiyoda-ku, Tokyo, Japan, hereby declare that I have a thorough knowledge of Japanese and English languages, and that the attached pages contain a correct translation into English of the priority documents of Japanese Patent Application No.2004-174788 filed on June 11, 2004 in the name of CANON KABUSHIKI KAISHA.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made, are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 8th day of December, 2008

A handwritten signature in black ink, appearing to read 'Shinichi Usui', is written over a horizontal line.

SHINICHI USUI

PATENT OFFICE
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This is to certify that the annexed is a true copy
of the following application as filed with this office.

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Applicant(s): CANON KABUSHIKI KAISHA

August 17, 2005

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Applicant's Information

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(Reason of Change) New Registration

Address: 3-30-2, Shimomaruko, Ohta-ku, Tokyo

Name: CANON KABUSHIKI KAISHA

日 本 国 特 許 庁
JAPAN PATENT OFFICE

別紙添付の書類に記載されている事項は下記の出願書類に記載されている事項と同一であることを証明する。

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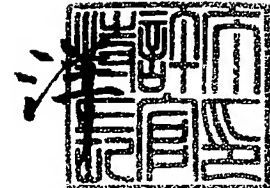
The country code and number
of your priority application,
to be used for filing abroad
under the Paris Convention, is

出 願 人
Applicant(s): キヤノン株式会社

2005年 8月17日

特許庁長官
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キャノン株式会社

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[Inventor]

[Domicile or Residence] c/o Canon Kabushiki Kaisha
30-2, 3-chome, Shimomaruko,
Ohta-ku, Tokyo

[Name] Takashi Kenmoku

[Inventor]

[Domicile or Residence] c/o Canon Kabushiki Kaisha
30-2, 3-chome, Shimomaruko,
Ohta-ku, Tokyo

[Name] Tatsuki Fukui

[Inventor]

[Domicile or Residence] c/o Canon Kabushiki Kaisha
30-2, 3-chome, Shimomaruko,
Ohta-ku, Tokyo

[Name] Chieko Mihara

[Inventor]

[Domicile or Residence] c/o Canon Kabushiki Kaisha
30-2, 3-chome, Shimomaruko,
Ohta-ku, Tokyo

[Name] Ako Kusakari

[Inventor]

[Domicile or Residence] c/o Canon Kabushiki Kaisha
30-2, 3-chome, Shimomaruko,
Ohta-ku, Tokyo

[Name] Tetsuya Yano

[Applicant]

[Identification No.] 000001007

[Name]	CANON KABUSHIKI KAISHA
[Attorney]	
[Identification No.]	100123788
[Patent Attorney]	
[Name]	Akio Miyazaki
[Telephone Number]	03-3585-1882
[Elected Attorney]	
[Identification No.]	100106297
[Patent Attorney]	
[Name]	Katsuhiro Ito
[Elected Attorney]	
[Identification No.]	100106138
[Patent Attorney]	
[Name]	Masayuki Ishibashi
[Indication of Official Fee]	
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[Material]	Abstract 1

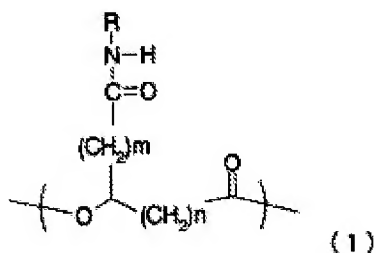
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[Name of the Document] Claim(s)

[Claim 1] Polyhydroxyalkanoate comprised of at
5 least a unit represented by chemical formula (1) within
the molecule:

[Chemical Formula 1]

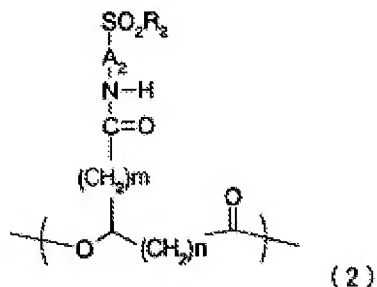


wherein R represents $-A_1-SO_2R_1$; R_1 represents OH, a
10 halogen atom, ONa, OK or OR_{1a} ; R_{1a} and A_1 each
independently represents a group having a substituted
or unsubstituted aliphatic hydrocarbon structure, a
substituted or unsubstituted aromatic ring structure or
a substituted or unsubstituted heterocyclic structure;
15 n represents an integer selected from 0 - 4; when n
represents an integer selected from 0, 2, 3, and 4, m
represents an integer selected from 0 - 8, and when n
is 0, m is 0; and in case plural units are present, R,
 R_1 , R_{1a} , A_1 , m and n have the aforementioned meanings
20 independently for each unit.

[Claim 2] Polyhydroxyalkanoate according to claim
1, comprised of, as the unit represented by chemical
formula (1), at least a unit represented by chemical

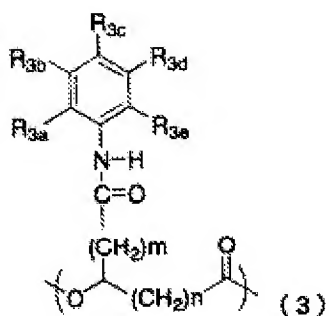
formula (2), chemical formula (3), chemical formula (4A) or (4B), within a molecule:

[Chemical Formula 2]



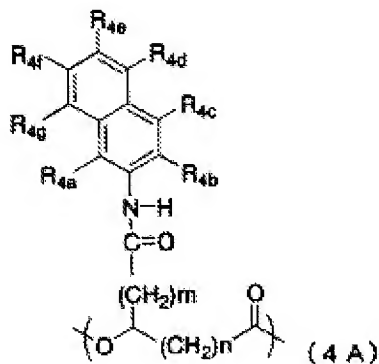
- 5 wherein R₂ represents OH, a halogen atom, ONa, OK or OR_{2a}; R_{2a} represents a linear or branched alkyl group with 1 to 8 carbon atoms or a substituted or unsubstituted phenyl group; A₂ represents a linear or branched alkylene group with 1 to 8 carbon atoms; n
- 10 represents an integer selected from 0 - 4; when n represents an integer selected from 0, 2, 3, and 4, m represents an integer selected from 0 - 8, and when n is 0, m is 0; and in case plural units are present, A₂, R₂, R_{2a}, m and n have the aforementioned meanings
- 15 independently for each unit;

[Chemical Formula 3]



wherein R_{3a} , R_{3b} , R_{3c} , R_{3d} and R_{3e} each independently represents SO_2R_{3f} (R_{3f} representing OH, a halogen atom, ONa, OK or OR_{3f1} (R_{3f1} representing a linear or branched alkyl group with 1 to 8 carbon atoms or a substituted or unsubstituted phenyl group)), a hydrogen atom, a halogen atom, an alkyl group with 1 - 20 carbon atoms, an alkoxy group with 1 - 20 carbon atoms, an OH group, an NH_2 group, an NO_2 group, $COOR_{3g}$ (R_{3g} representing a H atom, a Na atom or a K atom), an acetamide group, an OPh group, a NPh group, a CF_3 group, a C_2F_5 group or a C_3F_7 group (Ph indicating a phenyl group), of which at least one is SO_2R_{3f} ; n represents an integer selected from 0 - 4; when n represents an integer selected from 0, 2, 3, and 4, m represents an integer selected from 0 - 8, and when n is 0, m is 0; and in case plural units are present, R_{3a} , R_{3b} , R_{3c} , R_{3d} , R_{3e} , R_{3f} , R_{3f1} , R_{3g} , m and n have the aforementioned meanings independently for each unit;

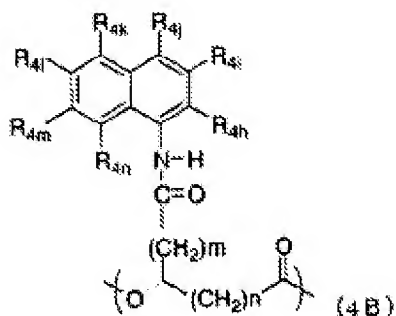
[Chemical Formula 4]



wherein R_{4a} , R_{4b} , R_{4c} , R_{4d} , R_{4e} , R_{4f} and R_{4g} each

independently represents SO_2R_{4o} (R_{4o} representing OH, a halogen atom, ONa, OK or OR_{4o1} (R_{4o1} representing a linear or branched alkyl group with 1 to 8 carbon atoms or a substituted or unsubstituted phenyl group)), a
5 hydrogen atom, a halogen atom, an alkyl group with 1 - 20 carbon atoms, an alkoxy group with 1 - 20 carbon atoms, an OH group, an NH_2 group, an NO_2 group, COOR_{4p} (R_{4p} representing a H atom, a Na atom or a K atom), an acetamide group, an OPh group, an NHPH group, a CF_3
10 group, a C_2F_5 group or a C_3F_7 group (Ph indicating a phenyl group), of which at least one is SO_2R_{4o} ; n represents an integer selected from 0 - 4; when n represents an integer selected from 0, 2, 3, and 4, m represents an integer selected from 0 - 8, and when n
15 is 0, m is 0; and in case plural units are present, R_{4a} , R_{4b} , R_{4c} , R_{4d} , R_{4e} , R_{4f} , R_{4g} , R_{4o} , R_{4o1} , R_{4p} , m and n have the aforementioned meanings independently for each unit;

[Chemical Formula 5]



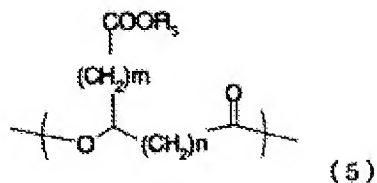
20

wherein R_{4h} , R_{4i} , R_{4j} , R_{4k} , R_{4l} , R_{4m} and R_{4n} each independently represents SO_2R_{4o} (R_{4o} representing OH, a

halogen atom, ONa, OK or OR_{4o1} (R_{4o1} representing a linear or branched alkyl group with 1 to 8 carbon atoms or a substituted or unsubstituted phenyl group)), a hydrogen atom, a halogen atom, an alkyl group with 1 - 20 carbon atoms, an alkoxy group with 1 - 20 carbon atoms, an OH group, an NH₂ group, an NO₂ group, COOR_{4p} (R_{4p} representing a H atom, a Na atom or a K atom), an acetamide group, an OPh group, an NHPPh group, a CF₃ group, a C₂F₅ group or a C₃F₇ group (Ph indicating a phenyl group), of which at least one is SO₂R_{4o}; n represents an integer selected from 0 - 4; when n represents an integer selected from 0, 2, 3, and 4, m represents an integer selected from 0 - 8, and when n is 0, m is 0; and in case plural units are present, R_{4h}, R_{4i}, R_{4j}, R_{4k}, R_{4l}, R_{4m}, R_{4n}, R_{4o}, R_{4o1}, R_{4p}, m and n have the aforementioned meanings independently for each unit.

[Claim 3] Polyhydroxyalkanoate comprised of at least a unit represented by chemical formula (5) within a molecule:

[Chemical Formula 6]

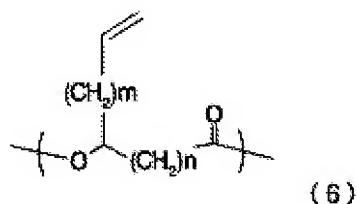


wherein R₅ represents hydrogen, a group capable of forming a salt or R_{5a}; R_{5a} represents a linear or

branched alkyl group with 1 - 12 carbon atoms, an
aralkyl group or a substituent having a sugar; n
represents an integer selected from 0 - 4; when n is 0,
m represents an integer selected from 2 - 8, however m
5 represents 2 only for R_{5a}, and when n represents an
integer selected from 2 - 4, m represents an integer
selected from 0 - 8; and in case plural units are
present, R₅, R_{5a}, m and n have the aforementioned
meanings independently for each unit.

10 [Claim 4] Polyhydroxyalkanoate comprised of at
least a unit represented by chemical formula (6) within
a molecule:

[Chemical Formula 7]

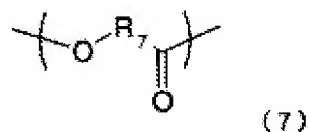


15 wherein n represents an integer selected from 0 - 4;
when n is 0, m represents an integer selected from 2 -
8, when n represents an integer selected from 2 - 3, m
represents an integer selected from 0 - 8, and when n
represents an integer selected from 2, m represents an
20 integer selected from 2 and 2 - 8; and in case plural
units are present, m and n have the aforementioned
meanings independently for each unit.

[Claim 5] Polyhydroxyalkanoate according to any
one of claims 1 to 4, further comprised of a unit

represented by chemical formula (7) within a molecule:

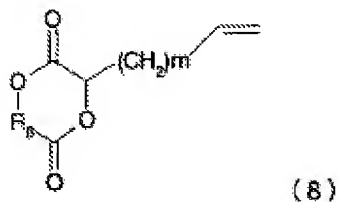
[Chemical Formula 8]



wherein R₇ represents a linear or branched alkylene
 5 with 1 - 11 carbon atoms, alkyleneoxyalkylene group
 (each alkylene group being independently with 1 - 2
 carbon atoms), a linear or branched alkenyl group with
 1 - 11 carbon atoms or an alkylidene group with 1 - 5
 carbon atoms which may be substituted with an aryl
 10 group; and in case plural units are present, R₇ has the
 aforementioned meanings independently for each unit.

[Claim 6] A method for producing a
 polyhydroxyalkanoate represented by chemical formula
 (9), comprised of a step of polymerizing a compound
 15 represented by chemical formula (8) in the presence of
 a catalyst:

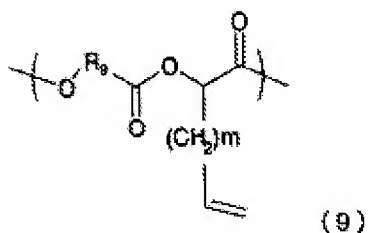
[Chemical Formula 9]



wherein R₈ represents a linear or branched alkylene
 20 with 1 - 11 carbon atoms, alkyleneoxyalkylene group
 (each alkylene group being independently with 1 - 2

carbon atoms), a linear or branched alkenyl group with 1 - 11 carbon atoms or an alkylidene group with 1 - 5 carbon atoms which may be substituted with an aryl group; and m represents an integer selected from 2 - 8:

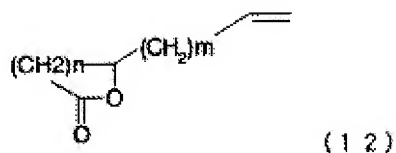
5 [Chemical Formula 10]



wherein R₉ represents a linear or branched alkylene with 1 - 11 carbon atoms, alkyleneoxyalkylene group (each alkylene group being independently with 1 - 2
10 carbon atoms), a linear or branched alkenyl group with 1 - 11 carbon atoms or an alkylidene group with 1 - 5 carbon atoms which may be substituted with an aryl group; m represents an integer selected from 2 - 8; and in case plural units are present, R₉ and m have the
15 aforementioned meanings independently for each unit.

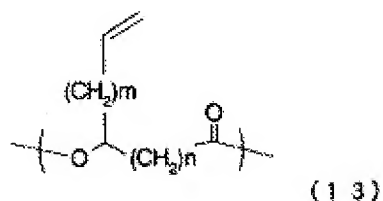
[Claim 7] A method for producing a polyhydroxyalkanoate represented by chemical formula (13), comprised of a step of polymerizing a compound represented by chemical formula (12) in the presence of
20 a catalyst:

[Chemical Formula 11]



wherein n represents an integer selected from 2 - 4;
 when n represents an integer selected from 2 - 3, m
 represents an integer selected from 0 - 8, and when n
 5 is 4, m represents an integer selected from 0 and 2 -
 8;

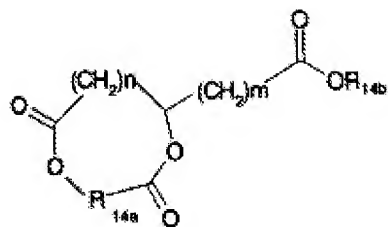
[Chemical Formula 12]



wherein n represents an integer selected from 2 - 4;
 10 when n represents an integer selected from 2 - 3, m
 represents an integer selected from 0 - 8, and when n
 is 4, m represents an integer selected from 0 and 2 -
 8; and in case plural units are present, m and n have
 the aforementioned meanings independently for each
 15 unit.

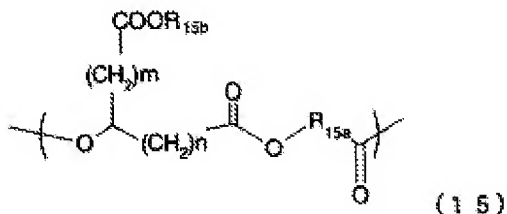
[Claim 8] A method for producing a
 polyhydroxyalkanoate represented by chemical formula
 (15), comprised of a step of polymerizing a compound
 represented by chemical formula (14) in the presence of
 20 a catalyst:

[Chemical Formula 13]



wherein R_{14a} represents a linear or branched alkylene group with 1 - 11 carbon atoms, alkyleneoxyalkylene group (each alkylene group being independently with 1 - 2 carbon atoms), a linear or branched alkenyl group with 1 - 11 carbon atoms or an alkylidene group with 1 - 5 carbon atoms which may be substituted with an aryl group; R_{14b} represents a linear or branched alkyl group with 1 - 12 carbon atoms or aralkyl group; and n represents an integer selected from 0, 2, 3 and 4; when n is 0, m represents an integer selected from 2 - 8, and when n is 2 - 4, m represents an integer selected from 0 - 8:

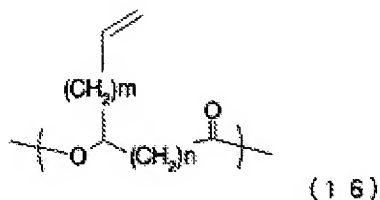
[Chemical Formula 14]



wherein R_{15a} represents a linear or branched alkylene with 1 - 11 carbon atoms, alkyleneoxyalkylene group (each alkylene group being independently with 1 - 2 carbon atoms), a linear or branched alkenyl group with 1 - 11 carbon atoms or an alkylidene group with 1 - 5

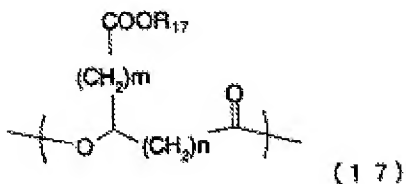
carbon atoms which may be substituted with an aryl group; R_{15b} represents a linear or branched alkyl group or aralkyl group; n represents an integer selected from 0, 2, 3 and 4; when n is 0, m represents an integer selected from 2 - 8, and when n is 2 - 4, m represents an integer selected from 0 - 8; and in case plural units are present, R_{15b} , m and n have the aforementioned meanings independently for each unit.

[Claim 9] A method for producing a polyhydroxyalkanoate comprising a unit represented by chemical formula (17), comprised of a step of oxidizing a double-bonded area of the polyhydroxyalkanoate comprising a unit represented by chemical formula (16):
[Chemical Formula 15]



wherein m represents an integer selected from 0 - 8; n is 0, 2, 3 or 4; and in case plural units are present, m and n have the aforementioned meanings independently for each unit;

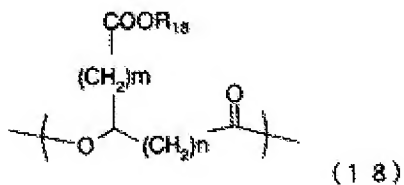
[Chemical Formula 16]



wherein m represents an integer selected from 0 - 8;
R₁₇ represents hydrogen, or a group capable of forming
a salt; n is 0, 2, 3 or 4; and in case plural units are
present, m, n and R₁₇ have the aforementioned meanings
5 independently for each unit.

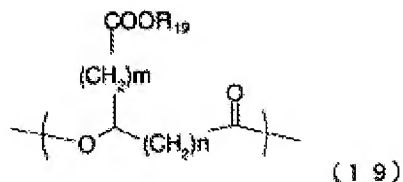
[Claim 10] A method for producing a
polyhydroxyalkanoate comprising a unit represented by
chemical formula (19), comprised of a step of executing
hydrolysis of a polyhydroxyalkanoate comprising a unit
10 represented by chemical formula (18) in the presence of
an acid or an alkali, or a step of executing
hydrogenolysis comprising a catalytic reduction:

[Chemical Formula 17]



15 wherein R₁₈ represents a linear or branched alkyl group
with 1 - 12 carbon atoms or an aralkyl group; n
represents an integer selected from 0, 2, 3 and 4; when
n is 0, m represents an integer selected from 2 - 8,
and when n is 2, 3 or 4, m represents an integer
20 selected from 0 - 8; and in case plural units are
present, R₁₈, m and n have the aforementioned meanings
independently for each unit:

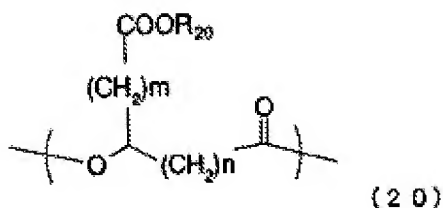
[Chemical Formula 18]



wherein R₁₉ represents hydrogen, or a group capable of forming a salt; n represents an integer selected from 0, 2, 3 and 4; when n is 0, m represents an integer selected from 2 - 8, and when n is 2, 3 or 4, m represents an integer selected from 0 - 8; and in case plural units are present, R₁₉, m and n have the aforementioned meanings independently for each unit.

[Claim 11] A method for producing a polyhydroxyalkanoate comprising a unit represented by chemical formula (1), comprised of a step of executing a condensation reaction of a polyhydroxyalkanoate comprising a unit represented by chemical formula (20) and an amine compound represented by chemical formula (21):

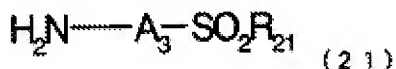
[Chemical Formula 19]



wherein R₂₀ represents hydrogen, or a group capable of forming a salt; n represents an integer selected from 0 - 4; when n is 0, 2, 3 or 4, m represents an integer selected from 0 - 8, when n is 1, m is 0; and in case

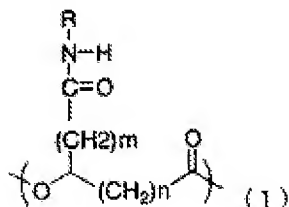
plural units are present, m, n and R₂₀ have the
aforementioned meanings independently for each unit;

[Chemical Formula 20]



- 5 wherein R₂₁ represents OH, a halogen atom, ONa, OK or
OR_{21a}; R_{21a} and A₃ each independently is selected from a
group having a substituted or unsubstituted aliphatic
hydrocarbon structure, a substituted or unsubstituted
aromatic ring structure, or a substituted or
10 unsubstituted heterocyclic structure; and in case
plural units are present, R₂₁, R_{21a} and A₃ have the
aforementioned meanings independently for each unit;

[chemical Formula 21]

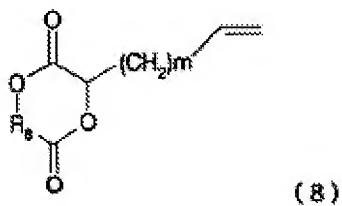


- 15 wherein R represents -A₁-SO₂R₁; R₁ represents OH, a
halogen atom, ONa, OK or OR_{1a}; R_{1a} and A₁ each
independently represents a group having a substituted
or unsubstituted aliphatic hydrocarbon structure, a
substituted or unsubstituted aromatic ring structure or
20 a substituted or unsubstituted heterocyclic structure;
n represents an integer selected from 0 - 4; when n is
0, 2 or 3, m represents an integer selected from 0 - 8,
and when n is 1, m is 0; and in case plural units are

present, R, R₁, R_{1a}, A₁, m and n have the aforementioned meanings independently for each unit.

[Claim 12] A compound represented by chemical formula (8):

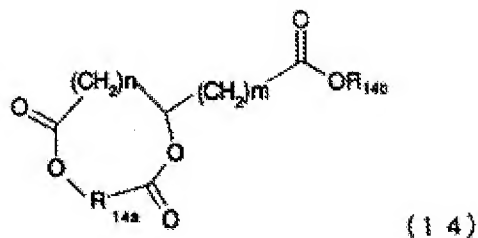
5 [Chemical Formula 22]



wherein R₈ represents a linear or branched alkylene with 1 - 11 carbon atoms, alkyleneoxyalkylene group (each alkylene group being independently with 1 - 2
 10 carbon atoms), a linear or branched alkenyl group with 1 - 11 carbon atoms or an alkylidene group with 1 - 5 carbon atoms which may be substituted with an aryl group; and m represents an integer selected from 2 - 8.

[Claim 13] A compound represented by chemical
 15 formula (14):

[Chemical Formula 23]



wherein R_{14a} represents a linear or branched alkylene group with 1 - 11 carbon atoms, alkyleneoxyalkylene
 20 group (each alkylene group being independently with 1 -

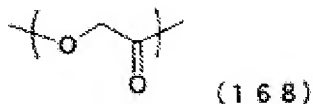
2 carbon atoms), a linear or branched alkenyl group with 1 - 11 carbon atoms or an alkylidene group with 1 - 5 carbon atoms which may be substituted with an aryl group; R_{14b} represents a linear or branched alkyl group or aralkyl group with 1 - 12 carbon atoms; and n represents an integer selected from 0, 2, 3 and 4; when n is 0, m represents an integer selected from 2 - 8, and when n is 2 - 4, m represents an integer selected from 0 - 8.

10 [Claim 14] A method for producing a polyhydroxyalkanoate comprising a unit represented by chemical formula (170), comprised of:

a step of reacting a polyhydroxyalkanoate comprising a unit represented by chemical formula (168) with a base; and

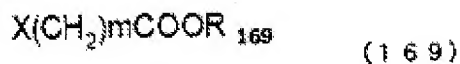
a step of reacting a compound obtained in the aforementioned step with a compound represented by chemical formula (169):

[Chemical Formula 24]



20

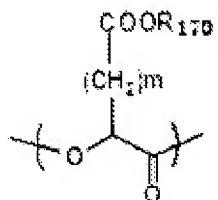
[Chemical Formula 25]



wherein m represents an integer selected from 0 - 8; X represents a halogen atom; and R₁₆₉ represents a linear

or branched alkyl group with 1 - 12 carbon atoms or an aralkyl group:

[Chemical Formula 26]



(170)

5 wherein m represents an integer selected from 0 - 8;
R₁₇₀ represents a linear or branched alkyl group with 1
- 12 carbon atoms or an aralkyl group; and in case
plural units are present, R₁₇₀ and m have the
aforementioned meanings independently for each unit.

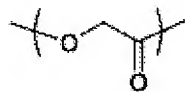
10 [Claim 15] A method for producing a
polyhydroxyalkanoate comprising a unit represented by
chemical formula (172), comprised of:

a step of reacting a polyhydroxyalkanoate
comprising a unit represented by chemical formula (168)

15 with a base; and

a step of reacting a compound obtained in the
aforementioned step with a compound represented by
chemical formula (171):

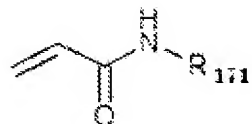
[Chemical Formula 27]



(168)

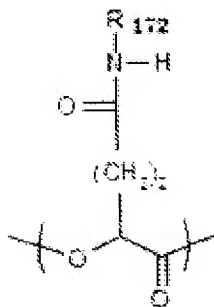
20

[Chemical Formula 28]



(171)

wherein R_{171} represents $-\text{A}_{14}-\text{SO}_2\text{R}_{171a}$; R_{171a} represents OH,
a halogen atom, ONa, OK or OR_{171b} ; R_{171b} and A_{171} each
independently is selected from a group having a
5 substituted or unsubstituted aliphatic hydrocarbon
structure, a substituted or unsubstituted aromatic ring
structure or a substituted or unsubstituted
heterocyclic structure; and in case plural units are
present, R_{171} , R_{171a} , R_{171b} , and A_{171} have the
10 aforementioned meanings independently for each unit;
[Chemical Formula 29]



(172)

wherein R_{172} represents $-\text{A}_{172}-\text{SO}_2\text{R}_{172a}$; R_{172a} represents OH,
a halogen atom, ONa, OK or OR_{172b} ; R_{172b} and A_{172} each
15 independently represents a group having a substituted
or unsubstituted aliphatic hydrocarbon structure, a
substituted or unsubstituted aromatic ring structure or
a substituted or unsubstituted heterocyclic structure;
and in case plural units are present, R_{172} , R_{172a} , R_{172b} ,

and A_{172} have the aforementioned meanings independently for each unit.

[Name of the Document] Specification

[Title of the Invention] Polyhydroxyalkanoic acid
having Vinyl, Ester, Carboxyl or Sulfonic Acid Group
and producing method therefor

5 [Technical Field]

[0001]

The present invention relates to a novel
polyhydroxyalkanoate and a producing method therefore.

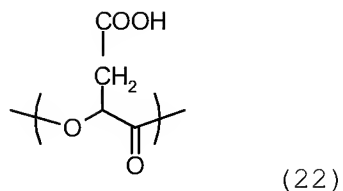
[Background Technology]

10 [0002]

Biodegradable polymer materials are widely
employed in medical materials, drug delivery systems,
environment-matching materials and the like. New
additional functions are recently required and various
15 researches are being made. Particularly in
polyhydroxyalkanoate represented by polylactic acid, an
introduction of a chemically modifiable functional
group into the molecule is investigated, and compounds
having a carboxyl group or a vinyl group are reported.
20 For example, polymalic acid is known as
polyhydroxyalkanoate having a carboxyl group in a side
chain. A polymer of polymalic acid is known, by a
manner of polymerization, in an α -type represented by
chemical formula (22):

25 [0003]

[Chemical Formula 1]

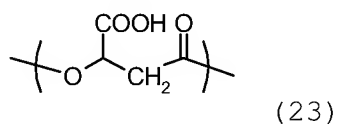


[0004]

and a β -type represented by chemical formula (23):

[0005]

5 [Chemical Formula 2]



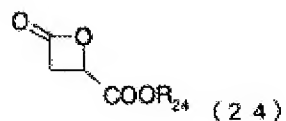
[0006]

Among these, as polymalic acid of β -type and a copolymer thereof, USP No. 4,265,247 (patent literature

10 1) discloses a polymer formed by a ring-opening polymerization of a benzyl ester of β -malolactone represented by chemical formula (24):

[0007]

[Chemical Formula 3]



15

[0008]

(R₂₄: benzyl group)

Also as a copolymer of α -type polymalic acid and glycolic acid and a copolymer containing other

20 hydroxyalkanoic acids other than glycolic acid,

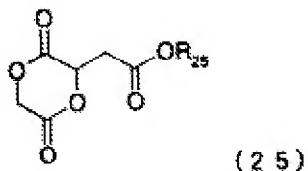
Japanese Patent Application Laid-open No. 2-3415

(patent literature 2) discloses a copolymer formed by a

6-membered ring diester monomer represented by chemical formula (25):

[0009]

[Chemical Formula 4]



5

[0010]

(R₂₅ being a lower alkyl group such as a methyl group, an ethyl group, an n-propyl group, an isopropyl group or a t-butyl group, or a benzyl group)

10 and a glycolide or a lactide which is a cyclic diester, or a lactone which is an intramolecular ring-closing ester of ω-hydroxycarboxylic acid.

[0011]

Also as a polyhydroxyalkanoate having a carboxyl
15 group in a side chain, Macromolecules 2000, 33 (13), 4619-4627 (non-patent literature 1) discloses a ring-opening polymerization of 7-oxo-4-oxepanonecarboxylic acid ester to form a polymer having an ester group in a side chain and a hydrogenolysis of the polymer to
20 obtain a polymer having a carboxylic acid in the side chain. Biomacromolecules 2000, 1, 275 (non-patent literature 2) discloses reacting poly(ε-caprolactone) with lithium diisopropylamide and then with benzyl chloroformate to obtain a polymer in which a

benzyloxycarbonyl group is introduced into an α -methylene group in a carbonyl group present in the main chain of poly(ϵ -caprolactone). Macromolecular Bioscience 2004, 4, 232 (non-patent literature 3)

5 discloses reacting polylactic acid with lithium diisopropylamide and then with benzyl bromoacetate to obtain a polymer in which a (benzyloxycarbonyl)methyl group is introduced into an α -methylene group in the carbonyl group present in the main chain of polylactic

10 acid. As a polyhydroxyalkanoate having a vinyl group in a side chain, Polymeric Materials Science & Engineering 2002, 87,254 (non-patent literature 4) discloses a polymer obtained by a ring-opening polymerization of α -allyl(δ -valerolactone). Also as a

15 polyhydroxyalkanoate similarly having a vinyl group in a side chain, Polymer Preprints 2002, 43(2), 727 (non-patent literature 5) discloses a polymer formed by a ring-opening polymerization of 3,6-diallyl-1,4-dioxane-2,5-dione which is a 6-membered ring diester monomer.

20 [0012]

Also there is reported a polymer having novel functions by introducing a structure providing a functionality into a polyhydroxyalkanoate in which a chemically modifiable functional group is introduced as

25 described above. International Journal of Biological Macromolecules 25 (1999) 265 (non-patent literature 6) discloses a ring-opening polymerization of a cyclic

dimer of α -malic acid and glycolic acid to obtain an α -malic acid-glycolic acid copolymer, and to unprotect the obtained polymer to obtain a polyester having a carboxyl group in a side chain. The carboxyl group of
5 the side chain is chemically modified with a tripeptide to obtain a polymer, which is reported to provide a satisfactory result in an evaluation of a cell adhesivity.

[Patent Literature 1] USP No. 4,265,247

10 [Patent Literature 2] Japanese Patent Application Laid-open No. 2-3415

[Non-patent Literature 1] Macromolecules 2000, 33 (13), 4619-4627

[Non-patent Literature 2] Biomacromolecules 2000,
15 1, 275

[Non-patent Literature 3] Macromolecular Bioscience 2004, 4, 232

[Non-patent Literature 4] Polymeric Materials Science & Engineering 2002, 87,254

20 [Non-patent Literature 5] Polymer Preprints 2002, 43(2), 727

[Non-patent Literature 6] International Journal of Biological Macromolecules 25 (1999) 265

[Disclosure of the Invention]

25 [Problem to be Solved by the Invention]

[0013]

Though it is conceived possible to obtain a new

functionality by introducing a unit having a carboxyl group or a unit having a vinyl group as a reactive functional group into the molecule and by chemically modifying such reactive functional group, but such reports are limited. Therefore, the present invention provides a novel polyhydroxyalkanoate having a reactive functional group in the molecule and a producing method therefor, and also to provide a novel polyhydroxyalkanoate having a novel function by chemically modifying polyhydroxyalkanoate having such reactive functional group and a producing method therefor.

[Means for Solving the Problem]

[0014]

The present inventors, as a result of intensive investigations for a novel polyhydroxyalkanoate having a reactive functional group in the molecule and for a novel polyhydroxyalkanoate having a novel function by chemically modifying the polyhydroxyalkanoate having such reactive functional group, have made the present invention.

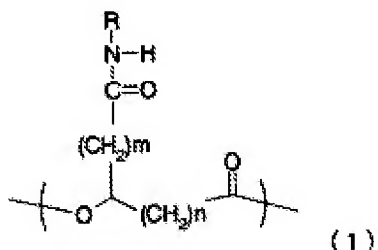
[0015]

According to an aspect of the present invention, there is provided following polyhydroxyalkanoate.

(1) Polyhydroxyalkanoate comprised of at least a unit represented by chemical formula (1) within the molecule:

[0016]

[Chemical Formula 5]



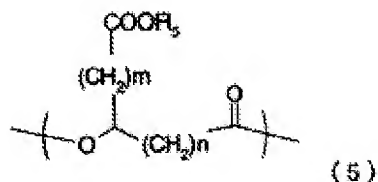
[0017]

- 5 wherein R represents $-A_1-SO_2R_1$; R_1 represents OH, a halogen atom, ONa, OK or OR_{1a} ; R_{1a} and A_1 each independently represents a group having a substituted or unsubstituted aliphatic hydrocarbon structure, a substituted or unsubstituted aromatic ring structure or
- 10 a substituted or unsubstituted heterocyclic structure; n represents an integer selected from 0 - 4; when n represents an integer selected from 0, 2, 3, and 4, m represents an integer selected from 0 - 8, and when n is 0, m is 0; and in case plural units are present, R,
- 15 R_1 , R_{1a} , A_1 , m and n have the aforementioned meanings independently for each unit.

(2) Polyhydroxyalkanoate comprised of at least a unit represented by chemical formula (5) within a molecule:

20 [0018]

[Chemical Formula 6]



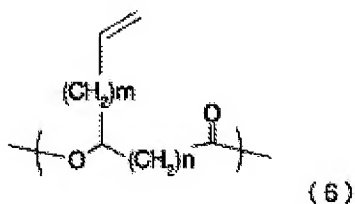
[0019]

wherein R_5 represents hydrogen, a group capable of forming a salt or R_{5a} ; R_{5a} represents a linear or
 5 branched alkyl group with 1 - 12 carbon atoms, an aralkyl group or a substituent having a sugar; n represents an integer selected from 0 - 4; when n is 0, m represents an integer selected from 2 - 8, however m represents 2 only for R_{5a} , and when n represents an
 10 integer selected from 2 - 4, m represents an integer selected from 0 - 8; and in case plural units are present, R_5 , R_{5a} , m and n have the aforementioned meanings independently for each unit.

(3) Polyhydroxyalkanoate comprised of at least a
 15 unit represented by chemical formula (6) within a molecule:

[0020]

[Chemical Formula 7]



20 [0021]

wherein n represents an integer selected from 0 - 4;

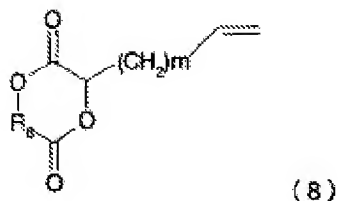
when n is 0, m represents an integer selected from 2 - 8, when n represents an integer selected from 2 - 3, m represents an integer selected from 0 - 8, and when n represents an integer selected from 2, m represents an integer selected from 2 and 2 - 8; and in case plural units are present, m and n have the aforementioned meanings independently for each unit.

According to a further aspect of the present invention, there are provided methods for producing a polyhydroxyalkanoate.

(A) A method for producing a polyhydroxyalkanoate represented by chemical formula (9), comprised of a step of polymerizing a compound represented by chemical formula (8) in the presence of a catalyst:

[0022]

[Chemical Formula 8]



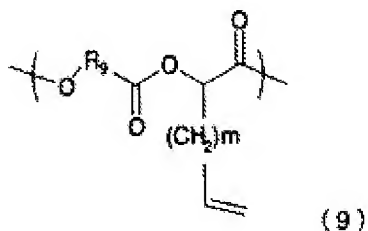
[0023]

wherein R_8 represents a linear or branched alkylene with 1 - 11 carbon atoms, alkyleneoxyalkylene group (each alkylene group being independently with 1 - 2 carbon atoms), a linear or branched alkenyl group with 1 - 11 carbon atoms or an alkylidene group with 1 - 5 carbon atoms which may be substituted with an aryl

group; and m represents an integer selected from 2 - 8;

[0024]

[Chemical Formula 9]



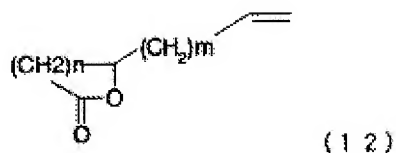
5 [0025]

wherein R₉ represents a linear or branched alkylene with 1 - 11 carbon atoms, alkyleneoxyalkylene group (each alkylene group being independently with 1 - 2 carbon atoms), a linear or branched alkenyl group with
10 1 - 11 carbon atoms or an alkylidene group with 1 - 5 carbon atoms which may be substituted with an aryl group; m represents an integer selected from 2 - 8; and in case plural units are present, R₉ and m have the aforementioned meanings independently for each unit.

15 (B) A method for producing a polyhydroxyalkanoate represented by chemical formula (13), comprised of a step of polymerizing a compound represented by chemical formula (12) in the presence of a catalyst:

[0026]

20 [Chemical Formula 10]

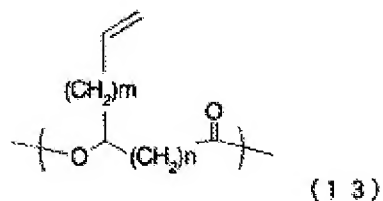


[0027]

wherein n represents an integer selected from 2 - 4;
 when n represents an integer selected from 2 - 3, m
 5 represents an integer selected from 0 - 8, and when n
 is 4, m represents an integer selected from 0 and 2 -
 8:

[0028]

[Chemical Formula 11]



10

[0029]

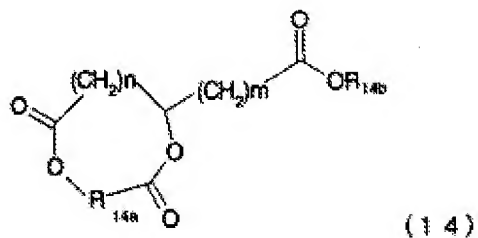
wherein n represents an integer selected from 2 - 4;
 when n represents an integer selected from 2 - 3, m
 represents an integer selected from 0 - 8, and when n
 15 is 4, m represents an integer selected from 0 and 2 -
 8; and in case plural units are present, m and n have
 the aforementioned meanings independently for each
 unit.

(C) A method for producing a polyhydroxyalkanoate
 20 represented by chemical formula (15), comprised of a
 step of polymerizing a compound represented by chemical

formula (14) in the presence of a catalyst:

[0030]

[Chemical Formula 12]

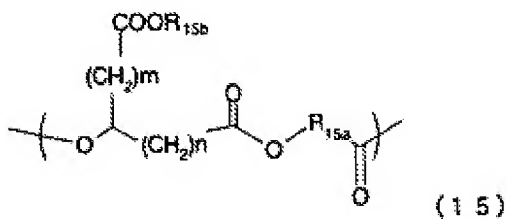


5 [0031]

wherein R_{14a} represents a linear or branched alkylene group with 1 - 11 carbon atoms, alkyleneoxyalkylene group (each alkylene group being independently with 1 - 2 carbon atoms), a linear or branched alkenyl group with 1 - 11 carbon atoms or an alkylidene group with 1 - 5 carbon atoms which may be substituted with an aryl group; R_{14b} represents a linear or branched alkyl group or aralkyl group with 1 - 12 carbon atoms; and n represents an integer selected from 0, 2, 3 and 4; when n is 0, m represents an integer selected from 2 - 8, and when n is 2 - 4, m represents an integer selected from 0 - 8;

[0032]

[Chemical Formula 13]



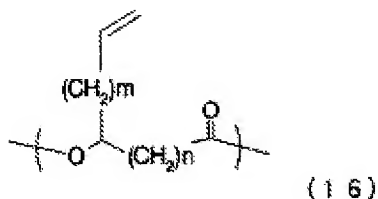
[0033]

wherein R_{15a} represents a linear or branched alkylene with 1 - 11 carbon atoms, alkyleneoxyalkylene group (each alkylene group being independently with 1 - 2
5 carbon atoms), a linear or branched alkenyl group with 1 - 11 carbon atoms or an alkylidene group with 1 - 5 carbon atoms which may be substituted with an aryl group; R_{15b} represents a linear or branched alkyl group or aralkyl group; n represents an integer selected from
10 0, 2, 3 and 4; when n is 0, m represents an integer selected from 2 - 8, and when n is 2 - 4, m represents an integer selected from 0 - 8; and in case plural units are present, R_{15b} , m and n have the aforementioned meanings independently for each unit.

15 (D) A method for producing a polyhydroxyalkanoate comprising a unit represented by chemical formula (17), comprised of a step of oxidizing a double-bonded area of the polyhydroxyalkanoate comprising a unit represented by chemical formula (16):

20 [0034]

[Chemical Formula 14]



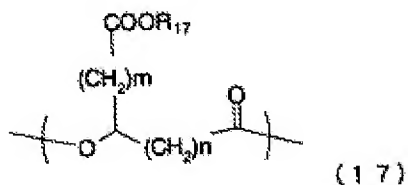
[0035]

wherein m represents an integer selected from 0 - 8; n

is 0, 2, 3 or 4; and in case plural units are present,
m and n have the aforementioned meanings independently
for each unit;

[0036]

5 [Chemical Formula 15]



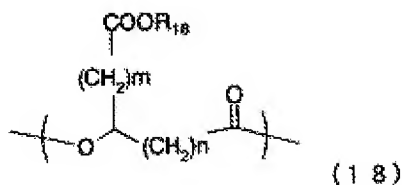
[0037]

wherein m represents an integer selected from 0 - 8;
R₁₇ represents hydrogen, or a group capable of forming
10 a salt; n is 0, 2, 3 or 4; and in case plural units are
present, m, n and R₁₇ have the aforementioned meanings
independently for each unit.

(E) A method for producing a polyhydroxyalkanoate
comprising a unit represented by chemical formula (19),
15 comprised of a step of executing hydrolysis of a
polyhydroxyalkanoate comprising a unit represented by
chemical formula (18) in the presence of an acid or an
alkali, or a step of executing hydrogenolysis
comprising a catalytic reduction:

20 [0038]

[Chemical Formula 16]



[0039]

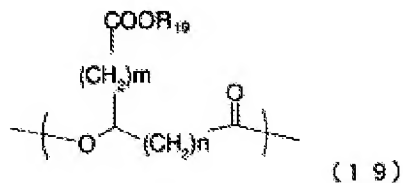
wherein R₁₈ represents a linear or branched alkyl group with 1 - 12 carbon atoms or an aralkyl group; n

5 represents an integer selected from 0, 2, 3 and 4; when n is 0, m represents an integer selected from 2 - 8, and when n is 2, 3 or 4, m represents an integer selected from 0 - 8; and in case plural units are

10 independently for each unit;

[0040]

[Chemical Formula 17]



[0041]

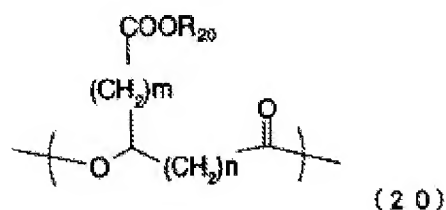
15 wherein R₁₉ represents hydrogen, or a group capable of forming a salt; n represents an integer selected from 0, 2, 3 and 4; when n is 0, m represents an integer selected from 2 - 8, and when n is 2, 3 or 4, m represents an integer selected from 0 - 8; and in case

20 plural units are present, R₁₉, m and n have the aforementioned meanings independently for each unit.

(F) A method for producing a polyhydroxyalkanoate comprising a unit represented by chemical formula (1), comprised of a step of executing a condensation reaction of a polyhydroxyalkanoate comprising a unit
 5 represented by chemical formula (20) and an amine compound represented by chemical formula (21):

[0042]

[Chemical Formula 18]

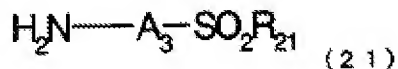


10 [0043]

wherein R_{20} represents hydrogen, or a group capable of forming a salt; n represents an integer selected from 0 - 4; when n is 0, 2, 3 or 4, m represents an integer selected from 0 - 8, when n is 1, m is 0; and in case
 15 plural units are present, m , n and R_{20} have the aforementioned meanings independently for each unit;

[0044]

[Chemical Formula 19]



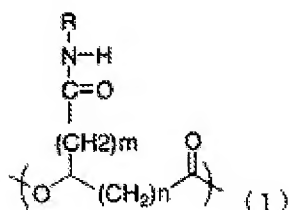
20 [0045]

wherein R_{21} represents OH, a halogen atom, ONa, OK or OR_{21a} ; R_{21a} and A_3 each independently is selected from a group having a substituted or unsubstituted aliphatic

hydrocarbon structure, a substituted or unsubstituted aromatic ring structure, or a substituted or unsubstituted heterocyclic structure; and in case plural units are present, R_{21} , R_{21a} and A_3 have the
 5 aforementioned meanings independently for each unit;

[0046]

[chemical Formula 20]



[0047]

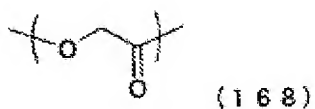
10 wherein R represents $-A_1-SO_2R_1$; R_1 represents OH, a halogen atom, ONa, OK or OR_{1a} ; R_{1a} and A_1 each independently represents a group having a substituted or unsubstituted aliphatic hydrocarbon structure, a substituted or unsubstituted aromatic ring structure or
 15 a substituted or unsubstituted heterocyclic structure; n represents an integer selected from 0 - 4; when n is 0, 2 or 3, m represents an integer selected from 0 - 8, and when n is 1, m is 0; and in case plural units are present, R, R_1 , R_{1a} , A_1 , m and n have the aforementioned
 20 meanings independently for each unit.

(G) A method for producing a polyhydroxyalkanoate comprising a unit represented by chemical formula (170), comprised of a step of reacting a polyhydroxyalkanoate comprising a unit represented by

chemical formula (168) with a base, and a step of reacting a compound obtained in the aforementioned step with a compound represented by chemical formula (169):

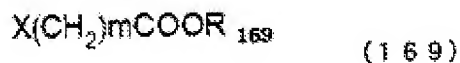
[0048]

5 [Chemical Formula 21]



[0049]

[Chemical Formula 22]

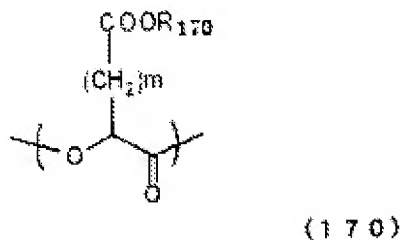


10 [0050]

wherein m represents an integer selected from 0 - 8; X represents a halogen atom; and R₁₆₉ represents a linear or branched alkyl group with 1 - 12 carbon atoms or an aralkyl group;

15 [0051]

[Chemical Formula 23]



[0052]

wherein m represents an integer selected from 0 - 8;

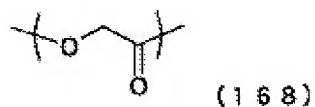
20 R₁₇₀ represents a linear or branched alkyl group with 1

- 12 carbon atoms or an aralkyl group; and in case plural units are present, R_{170} and m have the aforementioned meanings independently for each unit.

(H) A method for producing a polyhydroxyalkanoate comprising a unit represented by chemical formula (172), comprised of a step of reacting a polyhydroxyalkanoate comprising a unit represented by chemical formula (168) with a base, and a step of reacting a compound obtained in the aforementioned step with a compound represented by chemical formula (171):

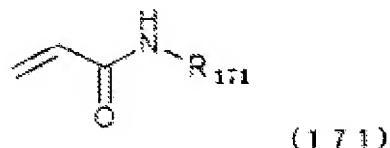
[0053]

[Chemical Formula 24]



[0054]

[Chemical Formula 25]



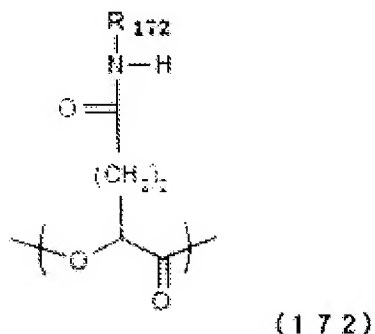
[0055]

wherein R_{171} represents $\text{---A}_{14}\text{---SO}_2\text{R}_{171a}$; R_{171a} represents OH, a halogen atom, ONa, OK or OR_{171b} ; R_{171b} and A_{171} each independently is selected from a group having a substituted or unsubstituted aliphatic hydrocarbon structure, a substituted or unsubstituted aromatic ring structure or a substituted or unsubstituted

heterocyclic structure; and in case plural units are present, R_{171} , R_{171a} , R_{171b} , and A_{171} have the aforementioned meanings independently for each unit;

[0056]

5 [Chemical Formula 26]



[0057]

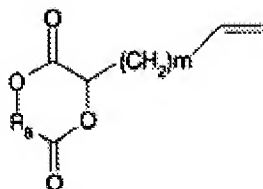
wherein R_{172} represents $-A_{172}-SO_2R_{172a}$; R_{172a} represents OH, a halogen atom, ONa, OK or OR_{172b} ; R_{172b} and A_{172} each
 10 independently represents a group having a substituted or unsubstituted aliphatic hydrocarbon structure, a substituted or unsubstituted aromatic ring structure or a substituted or unsubstituted heterocyclic structure;
 and in case plural units are present, R_{172} , R_{172a} , R_{172b} ,
 15 and A_{172} have the aforementioned meanings independently for each unit.

(I) A compound represented by chemical formula

(8):

[0058]

20 [Chemical Formula 27]



(8)

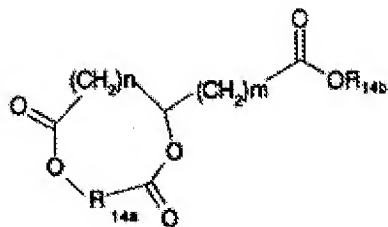
[0059]

wherein R₈ represents a linear or branched alkylene
with 1 - 11 carbon atoms, alkyleneoxyalkylene group
5 (each alkylene group being independently with 1 - 2
carbon atoms), a linear or branched alkenyl group with
1 - 11 carbon atoms or an alkylidene group with 1 - 5
carbon atoms which may be substituted with an aryl
group; and m represents an integer selected from 2 - 8.

10 (II) A compound represented by chemical formula
(14):

[0060]

[Chemical Formula 28]



(14)

15 [0061]

wherein R_{14a} represents a linear or branched alkylene
group with 1 - 11 carbon atoms, alkyleneoxyalkylene
group (each alkylene group being independently with 1 -
2 carbon atoms), a linear or branched alkenyl group
20 with 1 - 11 carbon atoms or an alkylidene group with 1

- 5 carbon atoms which may be substituted with an aryl group; R_{14b} represents a linear or branched alkyl group or aralkyl group with 1 - 12 carbon atoms; and n represents an integer selected from 0, 2, 3 and 4; when n is 0, m represents an integer selected from 2 - 8, and when n is 2 - 4, m represents an integer selected from 0 - 8.

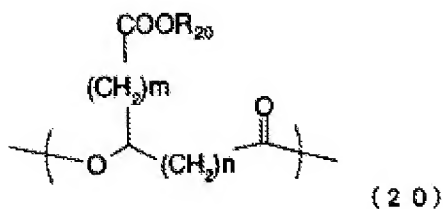
[0062]

[Best Mode for Carrying Out the Invention]

10 The present invention will be clarified in the following. A polyhydroxyalkanoate represented by chemical formula (1) and constituting the object of the invention can be produced by a reaction of a polyhydroxyalkanoate represented by chemical formula
15 (20) to be employed as a starting material, and at least an aminosulfonic acid represented by chemical formula (21).

[0063]

[Chemical Formula 29]



20

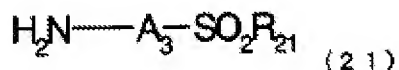
[0064]

wherein R_{20} represents hydrogen, or a group capable of forming a salt; n represents an integer selected from 0 - 4; when n is 0, 2, 3 or 4, m represents an integer

selected from 0 - 8, when n is 1, m is 0; and in case plural units are present, m, n and R₂₀ have the aforementioned meanings independently for each unit;

[0065]

5 [Chemical Formula 30]



[0066]

wherein R₂₁ represents OH, a halogen atom, ONa, OK or OR_{21a}; R_{21a} and A₃ each independently is selected from a group having a substituted or unsubstituted aliphatic hydrocarbon structure, a substituted or unsubstituted aromatic ring structure, or a substituted or unsubstituted heterocyclic structure; and in case plural units are present, R₂₁, R_{21a} and A₃ have the
10
15 aforementioned meanings independently for each unit.

More specifically, R₂₁ represents OH, a halogen atom, ONa, OK or OR_{21a}. R_{21a} represents a linear or branched alkyl group with 1 to 8 carbon atoms or a substituted or unsubstituted phenyl group

20 [0067]

A₃ is preferably a linear or branched, substituted or unsubstituted alkylene group with C₁ - C₈, a substituted or unsubstituted phenylene group, a substituted or unsubstituted naphthalene group, or a
25 substituted or unsubstituted group having a heterocyclic structure comprising at least one of N, S

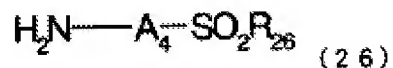
and O. In case A_3 has a cyclic structure, an unsubstituted ring may be further condensed. In case plural units are present, R_{21} , R_{21a} and A_3 have the aforementioned meanings independently for each unit.

5 [0068]

In case A_3 is a substituted or unsubstituted alkylene group, there can be employed an aminosulfonic acid represented by chemical formula (26):

[0069]

10 [Chemical Formula 31]



[0070]

wherein R_{26} represents OH, a halogen atom, ONa, OK or OR_{26a} ; R_{26a} represents a linear or branched alkyl group with 1 - 8 carbon atoms, or a substituted or unsubstituted phenyl group; A_4 represents a linear or branched, substituted or unsubstituted alkylene group with $C_1 - C_8$, and in case substituted, it may be substituted with an alkyl group with 1 - 20 carbon atoms or an alkoxy group with 1 - 20 carbon atoms.

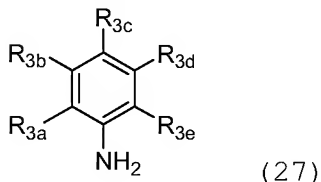
The compound represented by chemical formula (26) can be 2-aminoethanesulfonic acid (taurin), 3-aminopropanesulfonic acid, 4-aminobutanesulfonic acid, 2-amino-2-methylpropanesulfonic acid, or an alkali metal salt or an ester thereof.

[0071]

In case A₃ is a substituted or unsubstituted phenylene group, there can be employed an aminosulfonic acid compound represented by chemical formula (27):

[0072]

5 [Chemical Formula 32]



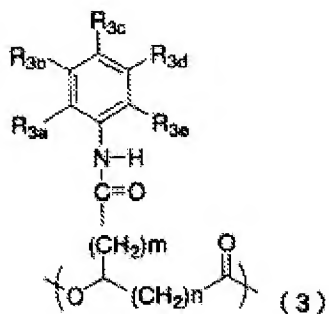
[0073]

wherein R_{3a}, R_{3b}, R_{3c}, R_{3d} and R_{3e} each independently represents SO₂R_{3f} (R_{3f} representing OH, a halogen atom, ONa, OK or OR_{3f1} (R_{3f1} representing a linear or branched alkyl group with 1 to 8 carbon atoms or a substituted or unsubstituted phenyl group)), a hydrogen atom, a halogen atom, an alkyl group with 1 - 20 carbon atoms, an alkoxy group with 1 - 20 carbon atoms, an OH group, 10 an NH₂ group, an NO₂ group, COOR_{3g} (R_{3g} representing a H atom, a Na atom or a K atom), an acetamide group, an OPh group, a NHPH group, a CF₃ group, a C₂F₅ group or a C₃F₇ group (Ph indicating a phenyl group), of which at least one is SO₂R_{3f}; and in case plural units are 15 present, R_{3a}, R_{3b}, R_{3c}, R_{3d}, R_{3e}, R_{3f}, R_{3f1}, and R_{3g}, have the aforementioned meanings independently for each unit.

The compound represented by chemical formula (27) allows to obtain a polyhydroxyalkanoate having at least 25 a unit represented by chemical formula (3):

[0074]

[Chemical Formula 33]



[0075]

5 wherein R_{3a} , R_{3b} , R_{3c} , R_{3d} , R_{3e} , n and m described in the formula have the aforementioned meanings.

The compound represented by chemical formula (27) can be p-aminobenzenesulfonic acid (sulfanylic acid), m-aminobenzenesulfonic acid, o-aminobenzenesulfonic acid, m-toluidine-4-sulfonic acid, o-toluidine-4-sulfonic acid sodium salt, p-toluidine-2-sulfonic acid, 4-methoxyaniline-2-sulfonic acid, o-anisidine-5-sulfonic acid, p-anisidine-3-sulfonic acid, 3-nitroaniline-4-sulfonic acid, 2-nitroaniline-4-sulfonic acid sodium salt, 4-nitroaniline-2-sulfonic acid sodium salt, 1,5-dinitroaniline-4-sulfonic acid, 2-aminophenol-4-hydroxy-5-nitrobenzenesulfonic acid, 2,4-dimethylaniline-5-sulfonic acid sodium salt, 2,4-dimethylaniline-6-sulfonic acid, 3,4-dimethylaniline-5-sulfonic acid, 4-isopropylaniline-6-sulfonic acid, 4-trifluoromethylaniline-6-sulfonic acid, 3-carboxy-4-

10
15
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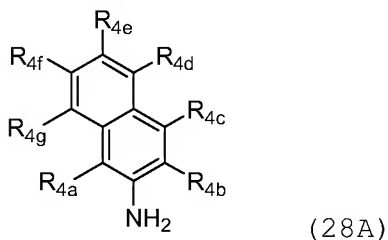
hydroxyaniline-5-sulfonic acid, 4-carboxyaniline-6-sulfonic acid, or an alkali metal salt or an ester thereof.

[0076]

5 In case A_3 is a substituted or unsubstituted naphthalene group, there can be employed an aminosulfonic acid compound represented by chemical formula (28A) or (28B):

[0077]

10 [Chemical Formula 34]

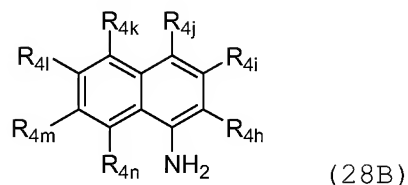


[0078]

wherein R_{4a} , R_{4b} , R_{4c} , R_{4d} , R_{4e} , R_{4f} and R_{4g} each independently represents SO_2R_{4o} (R_{4o} representing OH, a
15 halogen atom, ONa, OK or OR_{4o1} (R_{4o1} representing a linear or branched alkyl group with 1 to 8 carbon atoms or a substituted or unsubstituted phenyl group)), a
hydrogen atom, a halogen atom, an alkyl group with 1 -
20 carbon atoms, an alkoxy group with 1 - 20 carbon
20 atoms, an OH group, an NH_2 group, an NO_2 group, $COOR_{4p}$
(R_{4p} representing a H atom, a Na atom or a K atom), an acetamide group, an OPh group, an NHPH group, a CF_3 group, a C_2F_5 group or a C_3F_7 group (Ph indicating a phenyl group), of which at least one is SO_2R_{4o} :

[0079]

[Chemical Formula 35]



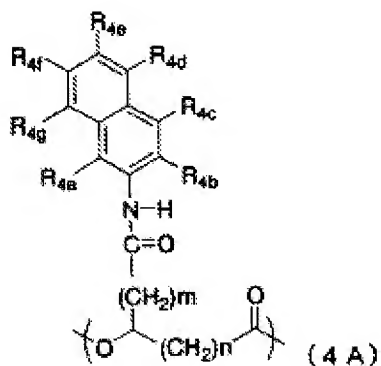
[0080]

5 wherein R_{4h} , R_{4i} , R_{4j} , R_{4k} , R_{4l} , R_{4m} and R_{4n} each independently represents SO_2R_{4o} (R_{4o} representing OH, a halogen atom, ONa, OK or OR_{4o1} (R_{4o1} representing a linear or branched alkyl group with 1 to 8 carbon atoms or a substituted or unsubstituted phenyl group)), a
 10 hydrogen atom, a halogen atom, an alkyl group with 1 - 20 carbon atoms, an alkoxy group with 1 - 20 carbon atoms, an OH group, an NH_2 group, an NO_2 group, $COOR_{4p}$ (R_{4p} representing a H atom, a Na atom or a K atom), an acetamide group, an OPh group, an NHPH group, a CF_3
 15 group, a C_2F_5 group or a C_3F_7 group (Ph indicating a phenyl group), of which at least one is SO_2R_{4o} .

The compound represented by chemical formula (28A) or (28B) allows to obtain a polyhydroxyalkanoate having at least a unit represented by chemical formula (4A) or
 20 (4B).

[0081]

[Chemical Formula 36]

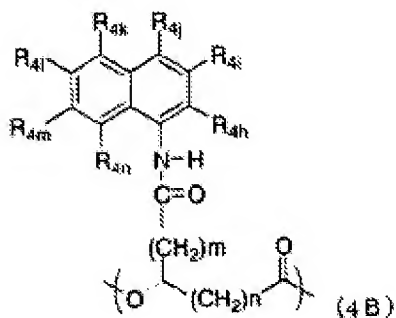


[0082]

wherein R_{4a} , R_{4b} , R_{4c} , R_{4d} , R_{4e} , R_{4f} , R_{4g} , n and m described in the formula have the aforementioned meanings.

[0083]

[Chemical Formula 37]



[0084]

wherein R_{4h} , R_{4i} , R_{4j} , R_{4k} , R_{4l} , R_{4m} , R_{4n} , n and m have the aforementioned meanings.

The compound represented by chemical formula (28A) or (28B) can be 1-naphthylamine-5-sulfonic acid, 1-naphthylamine-4-sulfonic acid, 1-naphthylamine-8-sulfonic acid, 2-naphthylamine-5-sulfonic acid, 1-naphthylamine-6-sulfonic acid, 1-naphthylamine-7-

sulfonic acid, 1-naphthylamine-2-ethoxy-6-sulfonic acid, 1-amino-2-naphthol-4-sulfonic acid, 6-amino-1-naphthol-3-sulfonic acid, 1-amino-8-naphthol-2,4-sulfonic acid monosodium salt, 1-amino-8-naphthol-3,6-sulfonic acid monosodium salt, or an alkali metal salt or ester thereof.

[0085]

In case A₃ represents a substituted or unsubstituted group having a heterocyclic structure comprising at least one of N, S and O, the heterocycle may be any of a pyridine ring, a piperazine ring, a furan ring and a thiol ring. The compound can be a sulfonic acid 2-aminopyridine-6-sulfonic acid or 2-aminopiperazine-6-sulfonic acid, or an alkali metal salt or ester thereof.

In case of a sulfonic acid ester, a group in an ester bonding with the sulfonic acid can be, as described above, a substituted or unsubstituted aliphatic hydrocarbon structure, a substituted or unsubstituted aromatic ring structure, or a substituted or unsubstituted heterocyclic structure. Also there is preferred a linear or branched alkyl group with 1 - 8 carbon atoms, or a substituted or unsubstituted phenyl group. In consideration for example of ease of esterification, there is further preferred OCH₃, OC₂H₅, OC₆H₅, OC₃H₇, OC₄H₉, OCH(CH₃)₂, OCH₂C(CH₃)₃, or OC(CH₃)₃.

[0086]

(Producing method for polyhydroxyalkanoate represented by chemical formula (1))

Now a reaction of the invention between a polyhydroxyalkanoate comprising a unit represented by
5 chemical formula (20) and the aminosulfonic acid compound represented by chemical formula (21) will be explained in detail. In the invention, the compound of chemical formula (21) is employed, with respect to the unit of chemical formula (20) employed as the starting
10 material, in an amount of 0.1 - 50.0 times in moles, preferably 1.0 - 20.0 times in moles.

[0087]

In the invention, an amide bond may be formed from a carboxylic acid and an amine for example by a
15 condensation reaction by a dehydration under heating. Particularly in consideration of a mild reaction condition not causing a cleavage of an ester bond in the main polymer chain, there is effectively employed a method of activating a carboxylic acid portion with an
20 activator to generate an active acyl intermediate, and then executing a reaction with an amine. The active acyl intermediate can be an acid halide, an acid anhydride or an active ester. In particular, a method of utilizing a condensing agent to form an amide bond
25 within a same reaction environment for simplifying the production process. It is also possible, if necessary, to once isolate an acid halide and then to execute a

condensation reaction with an amine.

[0088]

The condensing agent to be employed can be suitably selected for example from a phosphate
5 condensing agent employed in a polycondensation of an aromatic polyamide, a carbodiimide condensing agent employed in a peptide synthesis and an acid chloride condensing agent, depending on the compound of chemical formula (21) and the polyhydroxyalkanoate having the
10 unit shown in chemical formula (20).

[0089]

The phosphoric acid-based condensing agent can be a phosphite-based condensing agent, a phosphoric chloride-based condensing agent, a phosphoric
15 anhydride-based condensing agent, a phosphoric ester-based condensing agent, or a phosphoric amide-based condensing agent. In the reaction of the invention, a condensing agent such as a phosphite ester. The phosphite ester to be employed can be, for example,
20 triphenyl phosphite, diphenyl phosphite, tri-o-tolyl phosphite, tri-o-tolyl phosphite, tri-m-tolyl phosphite, di-m-tolyl phosphite, tri-p-tolyl phosphite, di-p-tolyl phosphite, di-o-chlorophenyl phosphite, tri-p-chlorophenyl phosphite, di-p-chlorophenyl phosphite,
25 trimethyl phosphite, or triethyl phosphite, among which triphenyl phosphite is employed preferably. Also for improving a solubility and a reactivity of polymer, a

metal salt such as lithium chloride or calcium chloride may be added.

[0090]

The carbodiimide condensing agent can be
5 dicyclohexyl carbodiimide (DCC), N-ethyl-N'-3-
dimethylaminopropyl carbodiimide (EDC=WSCI), or
diisopropyl carbodiimide (DIPC). DCC or WSCI may be
employed in combination with N-hydroxysuccinimide
(HONSu), 1-hydroxybenzotriazole (HOBt), or 3-hydroxy-4-
10 oxo-3,4-dihydro-1,2,3-benzotriazole (HOObt).

[0091]

The condensing agent is employed in an amount
within a range of 0.1 - 50 times in moles, preferably 1
- 20 moles with respect to the unit represented by
15 chemical formula (20).

[0092]

The reaction of the invention may employ a solvent
if necessary. The solvent to be employed can be a
hydrocarbon such as hexane, cyclohexane or heptane; a
20 ketone such as acetone or methyl ethyl ketone; an other
such as dimethyl ether, diethyl ether or
tetrahydrofuran; a halogenated hydrocarbon such as
dichloromethane, chloroform, carbon tetrachloride,
dichloroethane or trichloroethane; an aromatic
25 hydrocarbon such as benzene or toluene; a non-protonic
polar solvent such as N,N-dimethylformamide,
dimethylsulfoxide, dimethylacetamide, or

hexamethylphosphoramide; a pyridine derivative such as pyridine or picoline; or N-methylpyrrolidone.

Particularly preferably there is employed pyridine or N-methylpyrrolidone. An amount of the solvent may be

5 suitable determined according to a starting material, a type of base, reaction conditions and the like. In the method of the invention, a reaction temperature is not particularly restricted, but is usually within a range from -20°C to a boiling temperature of the solvent.

10 However the reaction is desirably executed at an optimum temperature matching the condensing agent to be employed.

[0093]

In the method of the invention, a reaction time is
15 usually within a range of 1 - 48 hours, preferably 1 - 10 hours.

[0094]

In the invention, a desired polyhydroxyalkanoate can be recovered and purified by an ordinary method
20 such as a distillation, from a reaction liquid containing thus generated polyhydroxyalkanoate having the unit represented in chemical formula (1).

Otherwise, the desired polyhydroxyalkanoate indicated by chemical formula (1) can be recovered by
25 precipitation by uniformly mixing the reaction liquid with a solvent for example water, an alcohol such as methanol or ethanol, or an ether such as dimethyl

ether, diethyl ether or tetrahydrofuran. If necessary,
polyhydroxyalkanoate having the unit represented by
chemical formula (1) may be isolated and purified.
Such isolation and purification are not particularly
5 restricted, and may be executed for example by a
precipitation with a solvent in which
polyhydroxyalkanoate is insoluble, a column
chromatography, or a dialysis.

Another producing method of the present invention,
10 in case a portion R in chemical formula (1) is $-A_1-$
 SO_3H , executes, after a condensation reaction with
amine, a methyl esterification with a methyl
esterifying agent to change the portion R in chemical
formula (1) into $-A_1-SO_3CH_3$. The methyl esterifying
15 agent can be that employed in a methyl esterification
of a fatty acid in a gas chromatography analysis. The
methyl esterification can be executed by an acid
catalyst method such as a hydrochloric acid-methanol
method, a boron trifluoride-methanol method or a
20 sulfuric acid-methanol method, or a base catalyst
method such as a sodium methoxide method, a tetramethyl
guanidine method or a trimethylsilyl diazomethane
method. Among these, the trimethylsilyl diazomethane
method is preferred as the methylation can be achieved
25 under a mild condition.

[0095]

The solvent to be employed in the reaction of the

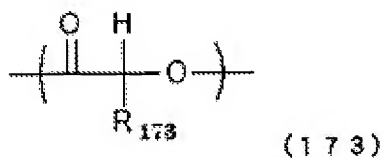
invention can be a hydrocarbon such as hexane,
cyclohexane or heptane; an alcohol such as methanol or
ethanol; a halogenated hydrocarbon such as
dichloromethane, chloroform, carbon tetrachloride,
5 dichloroethane or trichloroethane; or an aromatic
hydrocarbon such as benzene or toluene, particularly
preferably a halogenated hydrocarbon. An amount of the
solvent may be suitable determined according to a
starting material, reaction conditions and the like.
10 In the method of the invention, a reaction temperature
is not particularly restricted, but is usually within a
range from -20°C to 30°C. However the reaction is
desirably executed at an optimum temperature matching
the condensing agent and the reagents to be employed.

15 [0096]

Polyhydroxyalkanoate having a unit represented by
chemical formula (174) can be produced by a step of
reacting a polyhydroxyalkanoate having a unit
represented by chemical formula (173) with a base, and
20 a step of reacting a compound obtained in the
aforementioned step with a compound represented by
chemical formula (171).

[0097]

[Chemical Formula 38]



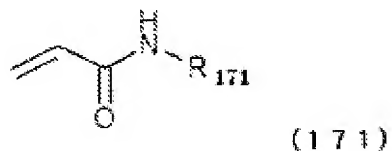
25

[0098]

wherein R_{173} represents a hydrogen atom, a linear or branched alkyl group, an aryl group, or an alkylidene group which may be substituted with an aryl group;

5 [0099]

[Chemical Formula 39]

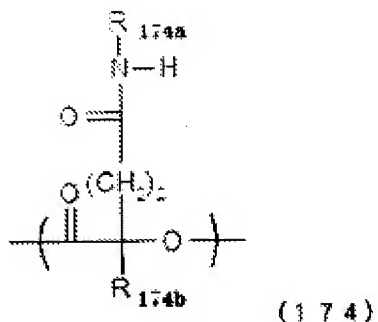


[0100]

wherein R_{171} represents $-A_{14}-SO_2R_{171a}$; R_{171a} represents OH,
10 a halogen atom, ONa, OK or OR_{171b} ; R_{171b} and A_{171} each independently is selected from a group having a substituted or unsubstituted aliphatic hydrocarbon structure, a substituted or unsubstituted aromatic ring structure or a substituted or unsubstituted
15 heterocyclic structure; and in case plural units are present, R_{171} , R_{171a} , R_{171b} , and A_{171} have the aforementioned meanings independently for each unit;

[0101]

[Chemical Formula 40]



[0102]

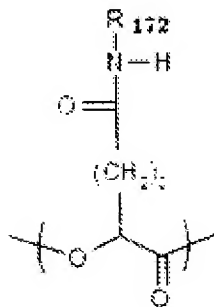
wherein R_{174a} represents $-A_{174}-SO_2R_{174c}$; R_{174c} represents OH, a halogen atom, ONa, OK or OR_{174d} ; R_{174d} and A_{174} each
 5 independently represents a group having a substituted or unsubstituted aliphatic hydrocarbon structure, a substituted or unsubstituted aromatic ring structure or a substituted or unsubstituted heterocyclic structure;
 R_{174b} represents a hydrogen atom, linear or branched
 10 alkyl group, aryl group, or alkylidene group which may be substituted with an aryl group; and in case plural units are present, R_{174a} , R_{174b} , R_{174c} , R_{174d} and A_{174} have the aforementioned meanings independently for each unit.

15 More specifically, in chemical formula (174), R_{174b} represents a hydrogen atom, and a polyhydroxyalkanoate comprising a unit represented by chemical formula (172) included in chemical formula (1) of the present invention can be produced by a step of reacting a
 20 polyhydroxyalkanoate having a unit represented by chemical formula (168) as a starting material with a base, and a step of reacting a compound obtained in the

aforementioned step with a compound represented by chemical formula (171).

[0103]

[Chemical Formula 41]



(172)

5

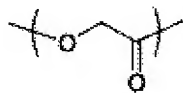
[0104]

wherein R_{172} represents $-\text{A}_{172}-\text{SO}_2\text{R}_{172a}$; R_{172a} represents OH, a halogen atom, ONa, OK or OR_{172b} ; R_{172b} and A_{172} each independently represents a group having a substituted or unsubstituted aliphatic hydrocarbon structure, a substituted or unsubstituted aromatic ring structure or a substituted or unsubstituted heterocyclic structure; and in case plural units are present, R_{172} , R_{172a} , R_{172b} , and A_{172} have the aforementioned meanings independently for each unit.

15

[0105]

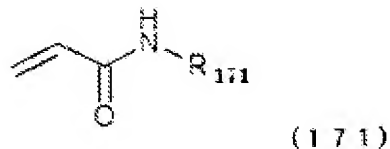
[Chemical Formula 42]



(168)

[0106]

20 [Chemical Formula 43]



[0107]

wherein R_{171} represents $-A_{14}-SO_2R_{171a}$; R_{171a} represents OH, a halogen atom, ONa, OK or OR_{171b} ; R_{171b} and A_{171} each
5 independently is selected from a group having a substituted or unsubstituted aliphatic hydrocarbon structure, a substituted or unsubstituted aromatic ring structure or a substituted or unsubstituted heterocyclic structure; and in case plural units are
10 present, R_{171} , R_{171a} , R_{171b} , and A_{171} have the aforementioned meanings independently for each unit.

A compound represented by chemical formula (171) can be 2-acrylamide-2-methylpropanesulfonic acid, an alkali metal salt thereof or an ester thereof.

15 [0108]

Now there will be explained the reaction between polyhydroxyalkanoate having a unit represented by chemical formula (168) and the compound represented by chemical formula (171).

20 [0109]

The present invention can be achieved by executing a Michael addition reaction of the compound represented by chemical formula (171) with an α -methine group adjacent to a carbonyl group in the polymer main chain.
25 More specifically, under a reaction condition of

Michael reaction, a polyhydroxyalkanoate having a unit represented by chemical formula (168) is reacted with a base capable of forming an anion in the α -methine group adjacent to a carbonyl group in the polymer main chain of the polyhydroxyalkanoate having the unit represented by chemical formula (168), and then with the compound represented by chemical formula (171). In the invention, the compound represented by chemical formula (171) is employed in an amount of 0.001 - 100 times in moles, preferably 0.01 - 10 times in moles, with respect to the unit represented by chemical formula (168).

[0110]

A solvent in the reaction of the invention is not particularly restricted as long as it is inert to the reaction and is capable of dissolving the starting material to a certain extent, but can be an aliphatic hydrocarbon such as hexane, cyclohexane, heptane, ligroin or petroleum ether; an aromatic hydrocarbon such as benzene, toluene or xylene; an ether such as diethyl ether, diisopropyl ether, tetrahydrofuran, dioxane, dimethoxyethane or diethylene glycol dimethyl ether; or an amide such as formamide, N,N-dimethylformamide, N,N-dimethylacetamide, N-methyl-2-pyrrolidone, N-methylpyrrolidone or hexamethylphosphorotriamide, preferably tetrahydrofuran.

[0111]

The reaction is executed in the presence of a base. The base to be employed can be an alkyl lithium such as methyl lithium or butyl lithium; an alkali metal disilazide such as lithium hexamethyl disilazide, 5 sodium hexamethyl disilazide, or potassium hexamethyl disilazide; or a lithium amide such as lithium diisopropylamide or lithium dicyclohexylamide, preferably lithium diisopropylamide. In the invention, the base is employed in an amount of 0.001 - 100 times 10 in moles, preferably 0.01 - 10 times in moles, with respect to the unit represented by chemical formula (168).

[0112]

In the method of the invention, a reaction 15 temperature is usually -78°C to 40°C , preferably -78°C to 30°C .

[0113]

In the method of the invention, a reaction time is usually within a range of 10 minutes to 24 hours, 20 preferably 10 minutes to 4 hours.

[0114]

On the other hand, in the polyhydroxyalkanoate having a unit represented by chemical formula (5) of the invention, a polyhydroxyalkanoate having a unit 25 represented by chemical formula (29) can be produced by a method of employing a polyhydroxyalkanoate having a unit represented by chemical formula (30) as a starting

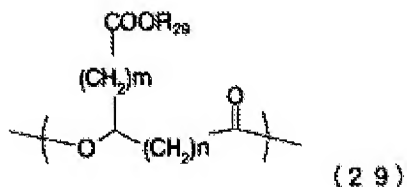
material and oxidizing a double-bonded area of the polyhydroxyalkanoate or employing a

polyhydroxyalkanoate having a unit represented by chemical formula (31) and hydrolyzing a side chain

5 ester portion in the presence of an acid or an alkali, or executing a hydrogenolysis comprising a catalytic reduction.

[0115]

[Chemical formula 44]



10

[0116]

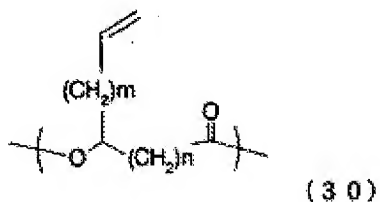
wherein R₂₉ represents hydrogen or a group capable of forming a salt; m represents an integer selected from 3

- 8; n is 0; and in case plural units are present, R₂₉,

15 m and n have the aforementioned meanings independently for each unit.

[0117]

[Chemical Formula 45]



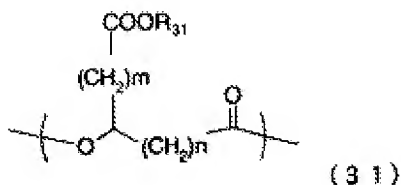
20 [0118]

wherein m represents an integer selected from 3 - 8; n

is 0; and in case plural units are present, m and n have the aforementioned meanings independently for each unit.

[0119]

5 [Chemical Formula 46]



[0120]

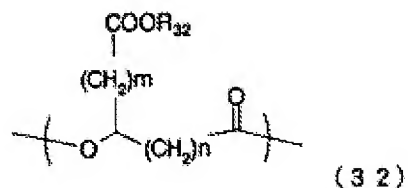
wherein R₃₁ represents a linear or branched alkyl group with 1 - 12 carbon atoms or an aralkyl group; m

10 represents an integer selected from 3 - 8, n is 0; and in case plural units are present, R₃₁, m and n have the aforementioned meanings independently for each unit.

Also, in the polyhydroxyalkanoate having a unit represented by chemical formula (5) of the invention, a
15 polyhydroxyalkanoate having a unit represented by chemical formula (32) can be produced by a method of employing a polyhydroxyalkanoate having a unit represented by chemical formula (33) as a starting material and oxidizing a double-bonded area or
20 employing a polyhydroxyalkanoate having a unit represented by chemical formula (34) and hydrolyzing a side chain ester portion in the presence of an acid or an alkali, or executing a hydrogenolysis comprising a catalytic reduction.

[0121]

[Chemical Formula 47]

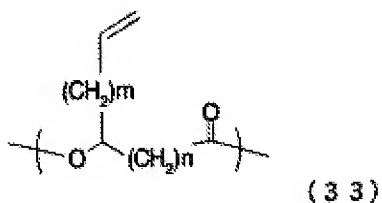


[0122]

5 wherein R₃₂ represents hydrogen or a group capable of forming a salt; m represents an integer selected from 0 - 8; n represents an integer selected from 2 - 4; and in case plural units are present, R₃₂, m and n have the aforementioned meanings independently for each unit.

10 [0123]

[Chemical Formula 48]

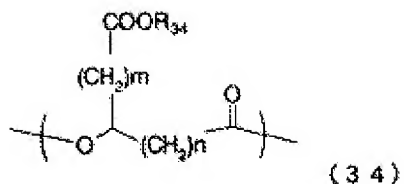


[0124]

15 wherein m represents an integer selected from 0 - 8; n represents an integer selected from 2 - 4; and in case plural units are present, m and n have the aforementioned meanings independently for each unit.

[0125]

[Chemical Formula 49]



[0126]

wherein R_{34} represents a linear or branched alkyl group with 1 - 12 carbon atoms or an aralkyl group; m

5 represents an integer selected from 0 - 8, n represents an integer selected from 2 - 4; and in case plural units are present, R_{34} , m and n have the aforementioned meanings independently for each unit.

(Producing methods for polyhydroxyalkanoate
10 represented by chemical formula (29) and chemical formula (32))

Now methods for producing a polyhydroxyalkanoate comprising a unit represented by chemical formula (29) from a polyhydroxyalkanoate comprising a unit
15 represented by chemical formula (30) of the present invention and a polyhydroxyalkanoate comprising a unit represented by chemical formula (32) from a polyhydroxyalkanoate comprising a unit represented by chemical formula (33) by an oxidation reaction will be
20 explained in detail.

[0127]

As a method of obtaining a carboxylic acid through oxidation cleavage of a double bonding of carbon-carbon using an oxidation agent, for example, a method using

permanganate (J. Chem. Soc., Perkin. Trans. 1, 806
(1973)), a method of using bichromate (Org. Synth., 4,
698 (1963)), a method of using periodate (J. Org.
Chem., 46, 19 (1981)), a method of using nitric acid
5 (Japanese Patent Application Laid-open No. 59-190945),
a method using ozone (J. Am. Chem. Soc., 81, 4273
(1959) and others are known. Furthermore,
Macromolecular chemistry, 4, 289-293 (2001) reports a
method of obtaining a carboxylic acid through the
10 reaction of a double bonding of carbon-carbon at the
end of a side chain of a polyhydroxyalkanoate produced
from a microorganism under acid conditions using
potassium permanganate as an oxidation agent. Also in
the present invention, the same methods can be used.

15 [0128]

As the permanganate used as an oxidation agent,
potassium permanganate is normally used. Since the
oxidation cleavage reaction is a stoichiometrical
reaction, the amount of potassium permanganate to be
20 used is normally 1 mol equivalent or more, preferably 2
- 10 mol equivalent, against 1 mol of a unit
represented by chemical formula (30) or (33).

[0129]

In order to make the reaction system under the
25 acid conditions, normally various types of inorganic
acids and organic acids, such as sulfuric acid,
hydrochloric acid, acetic acid and nitric acid are

used. However, when the acid, such as sulfuric acid, hydrochloric acid or acetic acid, is used, the ester bond of the main chain is broken, which may cause reduction of molecular weight. Because of this, it is preferable to use nitric acid. The amount of using the acid is normally 0.2 - 2000 mol equivalent, preferably 0.4 - 1000 mol equivalent, against 1 mol of a unit represented by chemical formula (30) or (33). When the amount exceeds 0.2 mol equivalent, the yield becomes desirable, and when the amount is below 2000 mol equivalent, reproduction of dissolved materials due to acid can be reduced, and therefore it is desirable to use within the above-mentioned range. Also, crown-ether may be used for the purpose of promoting the reaction. In this case, the effect, in which crown-ether and permanganate form a complex and increase the reaction activity, will be provided. As the crown-ether, dibenzo-18-crown-6-ether, dicyclo-18-crown-6-ether or 18-crown-6-ether is generally used. The amount of crown-ether to be used is normally 0.005 - 2.0 mol equivalent, preferably 0.01 - 1.5 mol equivalent, against 1 mol of permanganate.

[0130]

For a catalyst in the oxidation reaction of the present invention, as long as the catalyst is inactive to the reaction, there is no restriction. The catalyst to be employed can be, for example, water, acetone,

ethers such as tetrahydrofuran and dioxane, aromatic hydrocarbons such as benzene, aliphatic hydrocarbons such as hexane and heptane, or halogenated hydrocarbons such as methylchloride, dichloromethane and chloroform.

5 Among these catalysts, when considering the solubility of polyhydroxyalkanoate, halogenated hydrocarbons such as methylchloride, dichloromethane and chloroform and acetone are preferable.

[0131]

10 In the aforementioned oxidation reaction of the present invention, polyhydroxyalkanoate having a unit represented by chemical formula (30) or (33), permanganate and acid may be collectively prepared from the beginning together with the catalyst to react or
15 each may be added to the system continuously or intermittently to react. It is also possible to dissolve or suspend only the permanganate in the catalyst in advance and then add the polyhydroxyalkanoate and acid to the system
20 continuously or intermittently to react, or it is possible to dissolve or suspend only the polyhydroxyalkanoate in the catalyst in advance and then add the permanganate and acid to the system continuously or intermittently to react. Furthermore,
25 it is possible to prepare the polyhydroxyalkanoate and acid first and then add the permanganate to the system continuously or intermittently to react, or to prepare

the permanganate and acid first and then add the polyhydroxyalkanoate to the system continuously or intermittently to react. It is also possible to prepare the polyhydroxyalkanoate and permanganate first
5 and then add the acid to the system continuously or intermittently to react.

[0132]

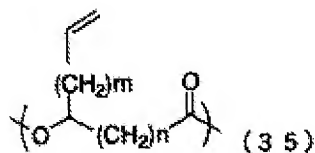
A reaction temperature is usually -40 to 40°C, preferably -10 to 30°C. The reaction time depends on
10 the stoichiometrical mixture ratio between a unit represented by chemical formula (30) or (33) and permanganate and the reaction temperature, but it is preferably 2 - 48 hours normally.

[0133]

15 The above-mentioned oxidation reaction may be applied to a method of producing a polyhydroxyalkanoate represented by chemical formula (36) from a polyhydroxyalkanoate represented by chemical formula (35) of the present invention by an oxidation reaction,
20 and this is a novel producing method of the present invention.

[0134]

[Chemical Formula 50]

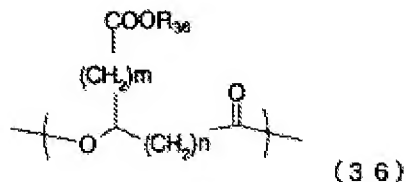


[0135]

wherein m represents 1 or 2 and n is 0.

[0136]

[Chemical Formula 51]



5

[0137]

wherein R₃₆ represents hydrogen, or a group capable of forming a salt; m represents 1 or 2; and n is 0.

In the following, there will be explained a method
10 of procuring a polyhydroxyalkanoate having a unit
represented by chemical formula (29) by a method of
employing a polyhydroxyalkanoate having a unit
represented by chemical formula (31) and hydrolyzing a
side chain ester portion thereof in the presence of an
15 acid or an alkali, or executing the hydrogenolysis
comprising a catalytic reduction, and a method of
procuring a polyhydroxyalkanoate having a unit
represented by chemical formula (32) by a method of
employing a polyhydroxyalkanoate having a unit
20 represented by chemical formula (34) and hydrolyzing a
side chain ester portion thereof in the presence of an
acid or an alkali, or executing the hydrogenolysis
comprising a catalytic reduction.

[0138]

In the method of hydrolysis in the presence of an acid or an alkali, there can be employed, in an aqueous solution or in a hydrophilic solvent such as methanol, ethanol, tetrahydrofuran, dioxane, dimethylformamide or
5 dimethylsulfoxide, an aqueous solution of an inorganic acid such as hydrochloric acid, sulfuric acid, nitric acid or phosphoric acid, or an organic acid such as trifluoroacetic acid, trichloroacetic acid, p-toluenesulfonic acid or methanesulfonic acid, an
10 aqueous solution of an aqueous caustic alkali such as sodium hydroxide or potassium hydroxide, or an aqueous solution of an alkali carbonate such as sodium carbonate or potassium carbonate, or an alcohol solution of a metal alkoxide such as sodium methoxide
15 or sodium ethoxide. A reaction temperature is usually 0 to 40°C, preferably 0 to 30°C. A reaction time is usually 0.5 to 48 hours. However a hydrolysis with any acid or alkali may cause a cleavage of the ester bond of the main chain, resulting in a decrease in the
20 molecular weight.

[0139]

Preparation of a carboxylic acid by hydrogenolysis comprising catalytic reduction is executed in the following manner. A catalytic reduction is executed by
25 reacting hydrogen under a normal or elevated pressure in a suitable solvent and in the presence of a reduction catalyst, at a temperature within a range of

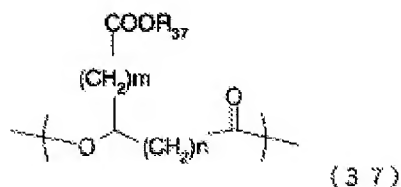
-20°C to the boiling point of the employed solvent, preferably 0 to 50°C. The solvent to be employed can be, for example, water, methanol, ethanol, propanol, hexafluoroisopropanol, ethyl acetate, diethyl ether, 5 tetrahydrofuran, dioxane, benzene, toluene, dimethylformamide, pyridine, or N-methylpyrrolidone. Also a mixture of these may also be employed. The reduction catalyst to be employed can be a single catalyst or a catalyst carried on a carrier, such as of 10 palladium, platinum, or rhodium, or Raney nickel. A reaction time is usually 0.5 to 72 hours. A reaction liquid containing thus generated polyhydroxyalkanoate having a unit represented by chemical formula (29) or (32) is subjected to a filtration for eliminating the 15 catalyst and a solvent elimination for example by a distillation to recover a crude polymer. The obtained polyhydroxyalkanoate having a unit represented by chemical formula (29) or (32) can be, if necessary, isolated and purified. Such isolation and purification 20 are not particularly restricted, and may be executed for example by a re-precipitation with a solvent in which the polyhydroxyalkanoate having a unit represented by chemical formula (29) or (32) is insoluble, a column chromatography, or a dialysis. 25 However even a catalytic reduction may also cause a cleavage of the ester bond of the main chain, resulting in a decrease in the molecular weight.

[0140]

Also in the polyhydroxyalkanoate having a unit represented by chemical formula (5) of the invention, a polyhydroxyalkanoate having a unit represented by chemical formula (37) can be produced by an esterification, employing a polyhydroxyalkanoate having a unit represented by chemical formula (24) as a starting material and employing an estifying agent.

[0141]

10 [Chemical Formula 52]

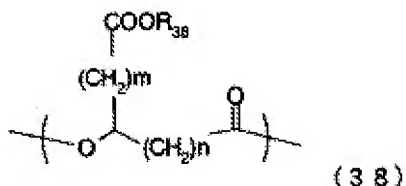


[0142]

wherein R_{37} represents a linear or branched alkyl group with 1 - 12 carbon atoms, an aralkyl group or a substituent having a sugar; n represents an integer selected from 0 - 4; when n is 0, m represents an integer selected from 2 - 8, and when n represents an integer selected from 2 - 4, m represents an integer selected from 0 - 8; and in case plural units are present, R_{37} , m and n have the aforementioned meanings independently for each unit:

[0143]

[Chemical Formula 53]



[0144]

wherein R_{38} represents hydrogen, or a group capable of forming a salt; n represents an integer selected from 0 - 4; when n is 0, m represents an integer selected from 2 - 8, and when n represents an integer selected from 2 - 4, m represents an integer selected from 0 - 8; and in case plural units are present, R_{38} , m and n have the aforementioned meanings independently for each unit.

As the esterifying agent, diazomethane and a DMF dimethylacetal can be employed. For example, a polyhydroxyalkanoate having a unit represented by chemical formula (38) easily reacts with trimethylsilyldiazomethane, DMF dimethyl acetal, DMF diethylacetal, DMF dipropylacetal, DMF-*t*-butylacetal, or DMF dineopentylacetal to provide a corresponding ester. Also an esterified polyhydroxyalkanoate can be obtained by a reaction, utilizing an acid catalyst or a condensing agent such as DCC, with an alcohol such as methanol, ethanol, propanol, isopropyl alcohol, butyl alcohol, sec-butyl alcohol, tert-butyl alcohol, pentyl alcohol, neopentyl alcohol, hexyl alcohol, heptyl alcohol, octyl alcohol, nonyl alcohol, decyl alcohol or lauryl alcohol, or with a sugar for introducing a sugar

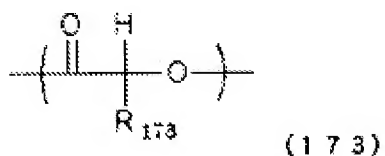
structure, such as D-glucose or D-fructose.

[0145]

Also a polyhydroxyalkanoate having a unit represented by chemical formula (175) can be produced by a step of reacting a polyhydroxyalkanoate having a unit represented by chemical formula (173) with a base, and a step of reacting a compound obtained in the aforementioned step with a compound represented by chemical formula (169).

10 [0146]

[Chemical Formula 54]

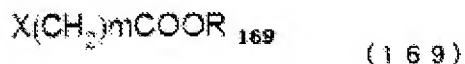


[0147]

wherein R_{173} represents a hydrogen atom, a linear or branched alkyl group, an aryl group, or an alkylidene group which may be substituted with an aryl group:

15 [0148]

[Chemical Formula 55]



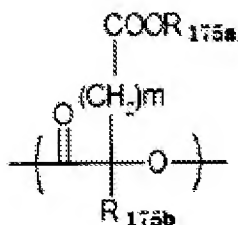
20 [0149]

wherein m represents an integer selected from 0 - 8; X represents a halogen atom; and R_{169} represents a linear or branched alkyl group with 1 - 12 carbon atoms or an

aralkyl group:

[0150]

[Chemical Formula 56]



(175)

5 [0151]

wherein m represents an integer selected from 0 - 8;

R_{175a} represents a linear or branched alkyl group with 1

- 12 carbon atoms or an aralkyl group; R_{175b} represents

a linear or branched alkyl group, an aryl group, or an

10 alkylidene group which may be substituted with an aryl

group; and in case plural units are present, R_{175a},

R_{175b}, m and n have the aforementioned meanings

independently for each unit.

More specifically, R_{Hb} is a hydrogen atom in

15 chemical formula (175), and the polyhydroxyalkanoate

having a unit represented by chemical formula (170) can

be produced by using the polyhydroxyalkanoate

represented by chemical formula (168) as a starting

material, and going through a step of reacting with a

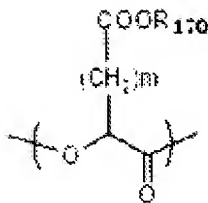
20 base and a step of reacting a compound obtained in the

aforementioned step with a compound represented by

chemical formula (169):

[0152]

[Chemical Formula 57]



(170)

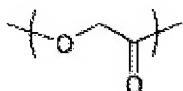
[0153]

wherein m represents an integer selected from 0 - 8;

- 5 R₁₇₀ represents a linear or branched alkyl group with 1 - 12 carbon atoms or an aralkyl group; and in case plural units are present, R₁₇₀ and m have the aforementioned meanings independently for each unit.

[0154]

- 10 [Chemical Formula 58]



(168)

[0155]

[Chemical Formula 59]



(169)

- 15 [0156]

wherein m represents an integer selected from 0 - 8; X represents a halogen atom; and R₁₆₉ represents a linear or branched alkyl group with 1 - 12 carbon atoms or an aralkyl group.

- 20 Examples of the compound represented by chemical

formula (169) include methyl chloroformate, ethyl
chloroformate, propyl chloroformate, isopropyl
chloroformate, butyl chloroformate, cyclohexyl
chloroformate, benzyl chloroformate, methyl
5 bromoformate, ethyl bromoformate, propyl bromoformate,
isopropyl bromoformate, butyl bromoformate, cyclohexyl
bromoformate, benzyl bromoformate, methyl
chloroacetate, ethyl chloroacetate, propyl
chloroacetate, isopropyl chloroacetate, butyl
10 chloroacetate, cyclohexyl chloroacetate, benzyl
chloroacetate, methyl bromoacetate, ethyl bromoacetate,
propyl bromoacetate, isopropyl bromoacetate, butyl
bromoacetate, cyclohexyl bromoacetate, benzyl
bromoacetate, methyl 3-chloropropionate, ethyl 3-
15 chloropropionate, propyl 3-chloropropionate, isopropyl
3-chloropropionate, butyl 3-chloropropionate,
cyclohexyl 3-chloropropionate, benzyl 3-
chloropropionate, methyl 3-bromopropionate, ethyl 3-
bromopropionate, propyl 3-bromopropionate, isopropyl 3-
20 bromopropionate, butyl 3-bromopropionate, cyclohexyl 3-
bromopropionate, benzyl 3-bromopropionate, methyl 4-
chlorobutyrate, ethyl 4-chlorobutyrate, propyl 4-
chlorobutyrate, isopropyl 4-chlorobutyrate, butyl 4-
chlorobutyrate, cyclohexyl 4-chlorobutyrate, benzyl 4-
25 chlorobutyrate, methyl 4-bromobutyrate, ethyl 4-
bromobutyrate, propyl 4-bromobutyrate, isopropyl 4-
bromobutyrate, butyl 4-bromobutyrate, cyclohexyl 4-

bromobutyrate, benzyl 4-bromobutyrate, methyl 5-
chlorovalerate, ethyl 5-chlorovalerate, propyl 5-
chlorovalerate, isopropyl 5-chlorovalerate, butyl 5-
chlorovalerate, cyclohexyl 5-chlorovalerate, benzyl 5-
5 chlorovalerate, methyl 5-bromovalerate, ethyl 5-
bromovalerate, propyl 5-bromovalerate, isopropyl 5-
bromovalerate, butyl 5-bromovalerate, cyclohexyl 5-
bromovalerate, benzyl 5-bromovalerate, methyl 6-
chlorohexanoate, ethyl 6-chlorohexanoate, propyl 6-
10 chlorohexanoate, isopropyl 6-chlorohexanoate, butyl 6-
chlorohexanoate, cyclohexyl 6-chlorohexanoate, benzyl
6-chlorohexanoate, methyl 6-bromohexanoate, ethyl 6-
bromohexanoate, propyl 6-bromohexanoate, isopropyl 6-
bromohexanoate, butyl 6-bromohexanoate, cyclohexyl 6-
15 bromohexanoate, benzyl 6-bromohexanoate, methyl 7-
chloroheptanoate, ethyl 7-chloroheptanoate, propyl 7-
chloroheptanoate, isopropyl 7-chloroheptanoate, butyl
7-chloroheptanoate, cyclohexyl 7-chloroheptanoate,
benzyl 7-chloroheptanoate, methyl 7-bromoheptanoate,
20 ethyl 7-bromoheptanoate, propyl 7-bromoheptanoate,
isopropyl 7-bromoheptanoate, butyl 7-bromoheptanoate,
cyclohexyl 7-bromoheptanoate, benzyl 7-bromoheptanoate,
methyl 8-chlorooctanoate, ethyl 8-chlorooctanoate,
propyl 8-chlorooctanoate, isopropyl 8-chlorooctanoate,
25 butyl 8-chlorooctanoate, cyclohexyl 8-chlorooctanoate,
benzyl 8-chlorooctanoate, methyl 8-bromooctanoate,
ethyl 8-bromooctanoate, propyl 8-bromooctanoate,

isopropyl 8-bromooctanoate, butyl 8-bromooctanoate,
cyclohexyl 8-bromooctanoate, benzyl 8-bromooctanoate,
methyl 9-chlorononanoate, ethyl 9-chlorononanoate,
propyl 9-chlorononanoate, isopropyl 9-chlorononanoate,
5 butyl 9-chlorononanoate, cyclohexyl 9-chlorononanoate,
benzyl 9-chlorononanoate, methyl 9-bromononanoate,
ethyl 9-bromononanoate, propyl 9-bromononanoate,
isopropyl 9-bromononanoate, butyl 9-bromononanoate,
cyclohexyl 9-bromononanoate, and benzyl 9-
10 bromononanoate.

[0157]

Now there will be explained the reaction between
polyhydroxyalkanoate having a unit represented by
chemical formula (168) and the compound represented by
15 chemical formula (169).

[0158]

The present invention can be achieved by executing
an addition reaction of the compound represented by
chemical formula (169) with an α -methine group adjacent
20 to a carbonyl group in the polymer main chain. More
specifically, under a condition of addition reaction, a
polyhydroxyalkanoate having a unit represented by
chemical formula (168) is reacted with a base capable
of forming an anion in the α -methine group adjacent to
25 a carbonyl group in the polymer main chain of the
polyhydroxyalkanoate having the unit represented by
chemical formula (168), and the compound represented by

chemical formula (169) is then reacted. In the invention, the compound represented by chemical formula (169) is employed in an amount of 0.001 - 100 times in moles, preferably 0.01 - 10 times in moles, with
5 respect to the unit represented by chemical formula (168).

[0159]

A solvent in the reaction of the invention is not particularly restricted as long as it is inert to the
10 reaction and is capable of dissolving the starting material to a certain extent, but can be an aliphatic hydrocarbon such as hexane, cyclohexane, heptane, ligroin or petroleum ether; an aromatic hydrocarbon such as benzene, toluene or xylene; an ether such as
15 diethyl ether, diisopropyl ether, tetrahydrofuran, dioxane, dimethoxyethane or diethylene glycol dimethyl ether; or an amide such as formamide, N,N-dimethylformamide, N,N-dimethylacetamide, N-methyl-2-pyrrolidone, N-methylpyrrolidone or hexamethyl
20 phosphorotriamide, preferably tetrahydrofuran.

[0160]

The reaction is executed in the presence of a base. The base to be employed can be an alkyl lithium such as methyl lithium or butyl lithium; an alkali
25 metal disilazide such as lithium hexamethyl disilazide, sodium hexamethyl disilazide, or potassium hexamethyl disilazide; or a lithium amide such as lithium

diisopropylamide or lithium dicyclohexylamide,
preferably lithium diisopropylamide. In the invention,
the base is employed in an amount of 0.001 - 100 times
in moles, preferably 0.01 - 10 times in moles, with
5 respect to the unit represented by chemical formula
(168).

[0161]

In the method of the invention, a reaction
temperature is usually -78°C to 40°C, preferably -78°C
10 to 30°C.

[0162]

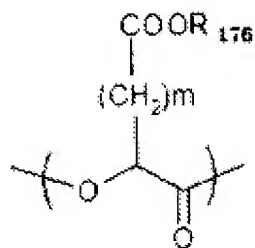
In the method of the invention, a reaction time is
usually within a range of 10 minutes to 24 hours,
preferably 10 minutes to 4 hours.

15 [0163]

In the method of the present invention, among
chemical formula (172), a compound represented by
chemical formula (176) included in chemical formula (5)
includes a novel compound of the present invention and
20 a method for producing that novel compound. Chemical
formula (177) shows a novel producing method of the
present invention.

[0164]

[Chemical Formula 60]



(176)

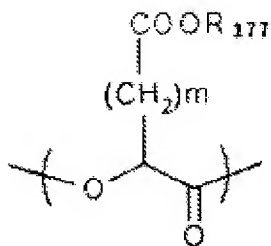
[0165]

wherein m represents an integer selected from 2 - 8;

R₁₇₆ represents a linear or branched alkyl group with 1
5 - 12 carbon atoms or aralkyl group; and in case plural
units are present, R₁₇₆ and m have the aforementioned
meanings independently for each unit.

[0166]

[Chemical Formula 61]



(177)

10

[0167]

wherein m represents an integer selected from 0 - 1;

R₁₇₇ represents a linear or branched alkyl group with 1
- 12 carbon atoms or aralkyl group; and in case plural
15 units are present, R₁₇₇ and m have the aforementioned
meanings independently for each unit.

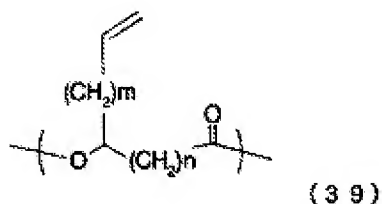
(Producing method of polyhydroxyalkanoate having a
unit represented by chemical formula (6))

(A) Producing method of polyhydroxyalkanoate having a unit represented by chemical formula (6) from a cyclic diester

In the polyhydroxyalkanoate having a unit represented by chemical formula (6) of the present invention, a polyhydroxyalkanoate having a unit represented by chemical formula (39) can be produced by polymerizing a compound represented by chemical formula (8) or (10) in the presence of a catalyst:

10 [0168]

[Chemical Formula 62]



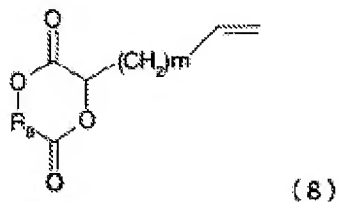
[0169]

wherein m is an integer selected from 2 - 8; n is 0;

15 and in case plural units are present, m and n have the aforementioned meanings independently for each unit.

[0170]

[Chemical Formula 63]



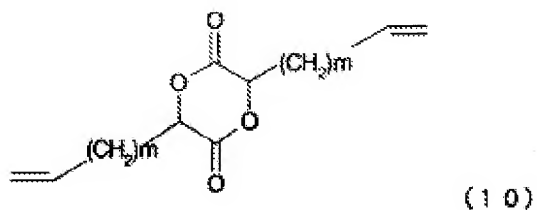
20 [0171]

wherein R₈ represents a linear or branched alkylene

with 1 - 11 carbon atoms, alkyleneoxyalkylene group
(each alkylene group being independently with 1 - 2
carbon atoms), a linear or branched alkenyl group with
1 - 11 carbon atoms or an alkylidene group with 1 - 5
5 carbon atoms which may be substituted with an aryl
group; and m represents an integer selected from 2 - 8:

[0172]

[Chemical Formula 64]



10 [0173]

wherein m represents an integer selected from 2 - 8.

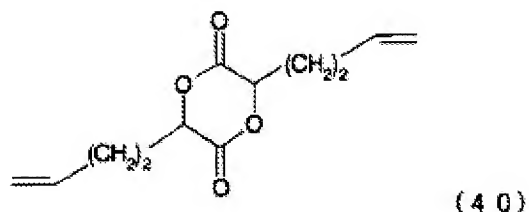
A compound represented by this chemical formula
(8) is a novel compound of the present invention. Now
there will be explained the synthesis method of a
15 compound (10), which is one of the compounds included
in the novel compounds (8) of the present invention.

(A) Producing method of a novel molecular cyclic
diester

A compound represented by chemical formula (40)
20 wherein $m = 2$, one of the novel compounds (10),

[0174]

[Chemical Formula 65]



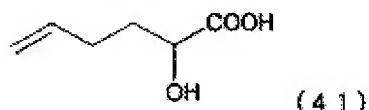
[0175]

can be obtained by a dehydration condensation of 2-hydroxy-5-hexene acid represented by chemical formula

5 (41):

[0176]

[Chemical Formula 66]



[0177]

10 The compound represented by chemical formula (40) can be obtained, for example, in a reactor equipped with a Dean-Stark trap, by subjecting a compound (41) and a catalyst promoting a dehydration condensation such as p-toluenesulfonic acid to an azeotropic

15 dehydration in toluene and under a nitrogen atmosphere for 24 hours or more and suitably removing the water accumulated in the Dean-Stark trap.

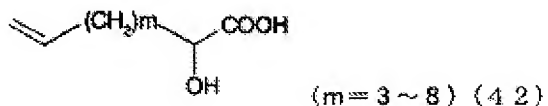
[0178]

20 In the same synthesis method mentioned above, using a compound represented by chemical formula (42), a compound of $m = 3 - 8$ represented by the

corresponding chemical formula (10) can be synthesized as well.

[0179]

[Chemical Formula 67]



5

[0180]

It is possible to move a step of producing a polyester constituted of a unit represented by chemical formula (39) using the molecular cyclic diester represented by the novel compound (8) produced as

10 mentioned above.

(B) Producing method of a polyester using a molecular cyclic diester

In the production of a polyester constituted of a unit represented by chemical formula (39) using the molecular cyclic diester represented by the novel compound (8) of the present invention, there is no restriction for the polymerization method. For example, solution polymerization, slurry polymerization

15 and mass polymerization may be used. When a polymerization solvent is used, there is no restriction for the solvent. For example, inert solvent such as aliphatic hydrocarbon or cyclic hydrocarbon with 5 - 18 carbon atoms and aromatic hydrocarbon with 6 - 20

20 carbons, tetrahydrofuran, chloroform,

25

orthodichlorobenzene or dioxane may be used.

[0181]

In the present invention, as a catalyst to be used for polymerization, there can be employed a known open-
5 ring polymerization catalyst for example tin dichloride, tin tetrachloride, stannous fluoride, stannous acetate, stannous stearate, stannous octanoate, stannous oxide, stannic oxide and other tin salts. Also, triethoxy aluminum, tri-n-propoxy-
10 aluminum, tri-iso-propoxy aluminum, tri-n-butoxy aluminum, tri-iso-butoxy aluminum, aluminum chloride, di-iso-propy zinc, dimethyl zinc, diethyl zinc, zinc chloride, tetra-n-propoxy titanium, tetra-n-butoxy titanium, tetra-t-butoxy titanium, antimony
15 trifluoride, oxidized salt, stearate, titanium tetrachloride, boron trifluoride, boron trifluoride ether complex, triethylamine or tributylamine can be listed. An amount of these catalysts is 0.0001 - 10 weight%, preferably 0.001 - 5 weight% with respect to
20 the total amount of the monomer compounds.

[0182]

In the present invention, for the ring-opening polymerization, there can be employed a known polymerization initiator. Specifically, for aliphatic
25 alcohol, any of mono-, di- and polyhydric-alcohols can be used, and both saturated and unsaturated alcohols are acceptable. For example, mono-alcohols such as

methanol, ethanol, propanol, butanol, pentanol,
hexanol, heptanol, nonanole, decanol, lauryl alcohol,
myristyl alcohol, cetyl alcohol, stearyl alcohol and p-
tert-benzyl alcohol, di-alcohols such as ethylene
5 glycol, butanediol, hexanediol, nonanediol and
tetramethylene glycol, polyhydric-alcohols such as
glycerol, sorbitol, xylitol, ribitol and erythritol),
methyl lactate and ethyl lactate are usable. These
aliphatic alcohols are used as the rate of 0.01 - 10
10 weight% with respect to the total amount of monomers,
although there are slight differenced depending on the
conditions, such as type of alcohol to be used.
[0183]

In the present invention, a ring-opening
15 polymerization reaction temperature is, in
consideration of a polymer generating speed and a
thermal composition rate of the generated polymer,
within a range of 100 - 200°C, preferably 120 - 180°C.
[0184]

20 In the present invention, the ring-opening
polymerization reaction can be executed under an inert
gas atmosphere, such as nitrogen or argon gas, or under
reduced or increased pressure, and a catalyst and
alcohol may be added gradually at that time.
25 [0185]

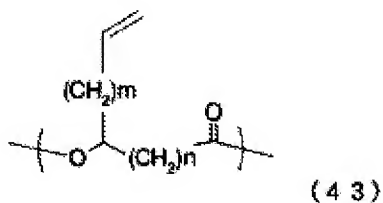
(B) Producing method to obtain a
polyhydroxyalkanoate having a unit represented by

chemical formula (6) from an intramolecular ring-closing compound of ω -hydroxycarboxylic acid

In a polyhydroxyalkanoate having a unit represented by chemical formula (6) of the present invention, a polyhydroxyalkanoate having a unit represented by chemical formula (43) can be produced by polymerizing an intramolecular ring-closing compound of ω -hydroxycarboxylic acid represented by chemical formula (12) in the presence of a catalyst.

10 [0186]

[Chemical Formula 68]



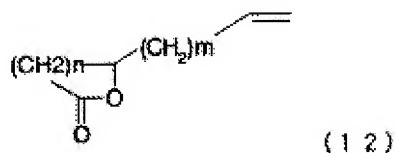
[0187]

wherein n represents an integer selected from 2 - 4;

15 when n represents an integer selected from 2 - 3, m represents an integer selected from 0 - 8, and n is 4, m represents an integer selected from 0 and 2 - 8; and in case plural units are present, m and n have the aforementioned meanings independently for each unit.

20 [0188]

[Chemical Formula 69]



[0189]

wherein n represents an integer selected from 2 - 4;

when n represents an integer selected from 2 - 3, m

5 represents an integer selected from 0 - 8, and when n

is 4, m represents an integer selected from 0 and 2 -

8.

In the production of a polyester constituted of a unit represented by chemical formula (39) using the

10 intramolecular ring-closing compound of ω -

hydroxycarboxylic acid represented by chemical formula

(12) of the present invention, there is no restriction

for the polymerization method. For example, solution polymerization, slurry polymerization and mass

15 polymerization may be used. When a polymerization

solvent is used, there is no restriction for the

solvent. For example, inert solvent such as aliphatic

hydrocarbon or cyclic hydrocarbon with 5 - 18 carbon

atoms and aromatic hydrocarbon with 6 - 20 carbons,

20 tetrahydrofuran, chloroform, orthodichlorobenzene or

dioxane may be used.

[0190]

In the present invention, as a catalyst to be used for polymerization, there can be employed a known open-

ring polymerization catalyst for example tin
dichloride, tin tetrachloride, stannous fluoride,
stannous acetate, stannous stearate, stannous
octanoate, stannous oxide, stannic oxide and other tin
5 salts. Also, triethoxy aluminum, tri-n-propoxy-
aluminum, tri-iso-propoxy aluminum, tri-n-butoxy
aluminum, tri-iso-butoxy aluminum, aluminum chloride,
di-iso-propy zinc, dimethyl zinc, diethyl zinc, zinc
chloride, tetra-n-propoxy titanium, tetra-n-butoxy
10 titanium, tetra-t-butoxy titanium, antimony
trifluoride, oxidized salt, stearate, titanium
tetrachloride, boron trifluoride, boron trifluoride
ether complex, triethylamine or tributylamine can be
listed. Di-iso-propy zinc, dimethyl zinc, diethyl zinc
15 and boron trifluoride, boron trifluoride ether complex
are preferably used.

[0191]

An amount of these catalysts is 0.0001 - 10
weight%, preferably 0.001 - 5 weight% with respect to
20 the total amount of the monomer compounds.

[0192]

In the present invention, for the ring-opening
polymerization, there can be employed a known
polymerization initiator. Specifically, for aliphatic
25 alcohol, any of mono-, di- and polyhydric-alcohols can
be used, and both saturated and unsaturated alcohols
are acceptable. For example, mono-alcohols such as

methanol, ethanol, propanol, butanol, pentanol,
hexanol, heptanol, nonanole, decanol, lauryl alcohol,
myristyl alcohol, cetyl alcohol, stearyl alcohol and p-
tert-benzyl alcohol, di-alcohols such as ethylene
5 glycol, butanediol, hexanediol, nonanediol and
tetramethylene glycol, polyhydric-alcohols such as
glycerol, sorbitol, xylitol, ribitol and erythritol),
methyl lactate and ethyl lactate are usable. These
aliphatic alcohols are used as the rate of 0.01 - 10
10 weight% with respect to the total amount of monomers,
although there are slight differenced depending on the
conditions, such as type of alcohol to be used. In the
present invention, a ring-opening polymerization
reaction temperature is within a range of 25 - 200°C,
15 preferably 50 - 200°C, more preferably 100 - 180°C.
[0193]

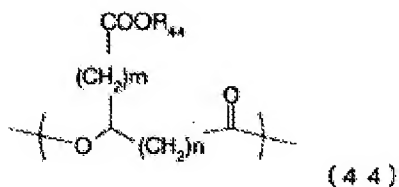
In the present invention, the ring-opening
polymerization reaction can be executed under an inert
gas atmosphere, such as nitrogen or argon gas, or under
20 reduced or increased pressure, and a catalyst and
alcohol may be added gradually at that time.
[0194]

Meanwhile, in the polyhydroxyalkanoate having a
unit represented by chemical formula (5) of the present
25 invention, a polyhydroxyalkanoate constituted of a unit
represented by chemical formula (44) can be produced by
the open-ring polymerization using a cyclic diester

compound, which is a novel compound represented by chemical formula (14), as a starting material.

[0195]

[Chemical Formula 70]



5

[0196]

wherein R_{44} represents a linear or branched alkyl group with 1 - 12 carbon atoms or an aralkyl group; n

represents an integer selected from 0, 2, 3 and 4; when

10 n is 0, m represents an integer selected from 2 - 8,

and when n represents an integer selected from 2 - 4, m

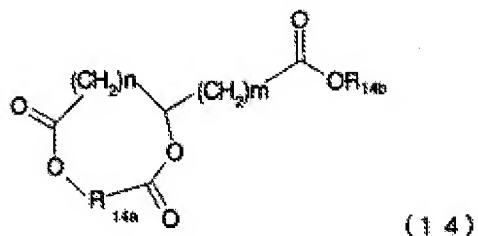
represents an integer selected from 2 - 8; and in case

plural units are present, R_{44} , m and n have the

aforementioned meanings independently for each unit.

15 [0197]

[Chemical Formula 71]



[0198]

wherein R_{14a} represents a linear or branched alkylene

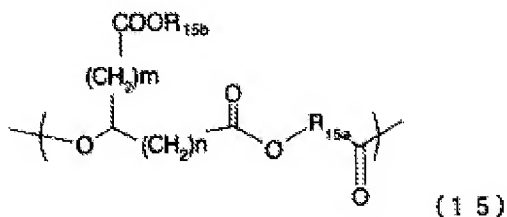
20 group with 1 - 11 carbon atoms, alkyleneoxyalkylene

group (each alkylene group being independently with 1 -
2 carbon atoms), a linear or branched alkenyl group
with 1 - 11 carbon atoms or an alkylidene group with 1
- 5 carbon atoms which may be substituted with an aryl
5 group; R_{14b} represents a linear or branched alkyl group
with 1 - 12 carbon atoms or an alkyl group; and n
represents an integer selected from 0, 2, 3 and 4; when
 n is 0, m represents an integer selected from 2 - 8,
and when n is 2 - 4, m represents an integer selected
10 from 0 - 8.

In this case, the unit of the polyhydroxyalkanoate
to be synthesized has a structure made of a repeat unit
represented by chemical formula (15).

[0199]

15 [Chemical Formula 72]



[0200]

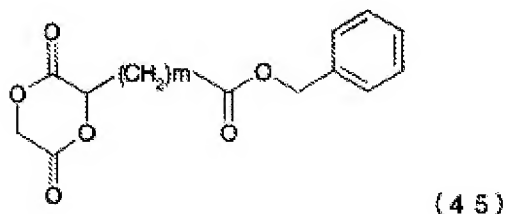
wherein R_{15a} represents a linear or branched alkylene
with 1 - 11 carbon atoms, alkyleneoxyalkylene group
20 (each alkylene group being independently with 1 - 2
carbon atoms), a linear or branched alkenyl group with
1 - 11 carbon atoms or an alkylidene group with 1 - 5
carbon atoms which may be substituted with an aryl

group; R_{15b} represents a linear or branched alkyl group or aralkyl group; n represents an integer selected from 0, 2, 3 and 4; when n is 0, m represents an integer selected from 2 - 8, and when n is 2 - 4, m represents
5 an integer selected from 0 - 8; and in case plural units are present, R_{15b} , m and n have the aforementioned meanings independently for each unit.

A compound represented by this chemical formula (14) is a novel compound of the present invention. Now
10 there will be explained the synthesis method of a compound (45) represented by chemical formula (45), which is one of the compounds included in the novel compounds (14) of the present invention.

[0201]

15 [Chemical Formula 73]



[0202]

wherein m represents an integer selected from 2 - 8.

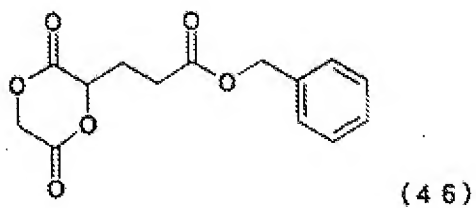
(A) Producing method of a novel molecular cyclic
20 diester

Now there will be explained the synthesis method of a compound represented by chemical formula (45), which is one of the compounds included in the novel

compounds (14) of the present invention. For example,
L-3-(2-benzyloxycarbonyl)ethyl-1, 4-dioxane-2, 5-dione
represented by chemical formula (46) wherein $m = 2$ can
be synthesized from L-glutamine acid as a starting
5 material. Specifically, a carboxyl group in γ -position
of L-glutamine acid is estrified as a compound
represented by chemical formula (47) using benzyl
alcohol. Next, the diazo hydrolytic cleavage is
executed, thereby converting an amino group to a
10 hydroxyl group like a compound represented by chemical
formula (48). Then, under ether or aromatic
hydrocarbon, preferably diethyl ether, as a catalyst,
for example, in the presence of a base such as
triethylamine, the coupling reaction is executed with
15 bromoacetyl chloride to obtain a compound represented
by chemical formula (49). Furthermore, under aprotic
polar solvent such as dimethylformamide or N-
methylpyrrolidone, as the solvent, the intramolecular
cyclization is executed using sodium hydrogencarbonate,
20 thereby being able to obtain L-3-(2-
benzyloxycarbonyl)ethyl-1, 4-dioxane-2, 5-dione.

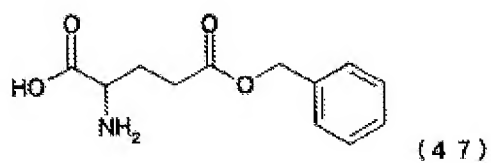
[0203]

[Chemical Formula 74]



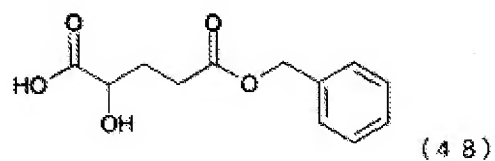
[0204]

[Chemical Formula 75]



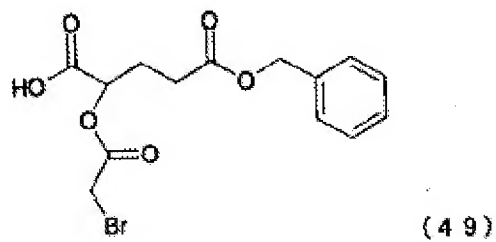
5 [0205]

[Chemical Formula 76]



[0206]

[Chemical Formula 77]



10

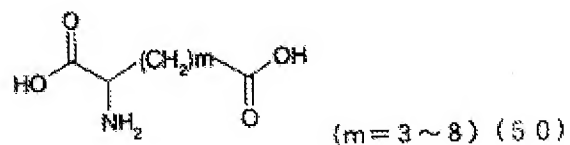
[0207]

In the same synthesis method mentioned above,
using a compound represented by chemical formula (50),

a compound wherein $m = 3 - 8$ represented by the corresponding chemical formula (45) can be synthesized as well.

[0208]

5 [Chemical Formula 78]



[0209]

It is possible to move a step of producing a polyester constituted of a unit represented by chemical
10 formula (44) using the molecular cyclic diester represented by the novel compound (14) produced as mentioned above.

(B) Producing method of a polyester using a molecular cyclic diester

15 In the production of a polyester constituted of a unit represented by chemical formula (44) using the molecular cyclic diester represented by the novel compound (14) of the present invention, there is no restriction for the polymerization method. For
20 example, solution polymerization, slurry polymerization and mass polymerization may be used. When a polymerization solvent is used, there is no restriction for the solvent. For example, inert solvent such as aliphatic hydrocarbon or cyclic hydrocarbon with 5 - 18

carbon atoms and aromatic hydrocarbon with 6 - 20
carbons, tetrahydrofuran, chloroform,
orthodichlorobenzene or dioxane may be used.
[0210]

5 In the present invention, as a catalyst to be used
for polymerization, there can be employed a known open-
ring polymerization catalyst for example tin
dichloride, tin tetrachloride, stannous fluoride,
stannous acetate, stannous stearate, stannous
10 octanoate, stannous oxide, stannic oxide and other tin
salts. Also, triethoxy aluminum, tri-n-propoxy-
aluminum, tri-iso-propoxy aluminum, tri-n-butoxy
aluminum, tri-iso-butoxy aluminum, aluminum chloride,
di-iso-propy zinc, dimethyl zinc, diethyl zinc, zinc
15 chloride, tetra-n-propoxy titanium, tetra-n-butoxy
titanium, tetra-t-butoxy titanium, antimony
trifluoride, oxidized salt, stearate, titanium
tetrachloride, boron trifluoride, boron trifluoride
ether complex, triethylamine or tributylamine can be
20 listed. An amount of these catalysts is 0.0001 - 10
weight%, preferably 0.001 - 5 weight% with respect to
the total amount of the monomer compounds.
[0211]

 In the present invention, for the ring-opening
25 polymerization, there can be employed a known
polymerization initiator. Specifically, for aliphatic
alcohol, any of mono-, di- and polyhydric-alcohols can

be used, and both saturated and unsaturated alcohols are acceptable. For example, mono-alcohols such as methanol, ethanol, propanol, butanol, pentanol, hexanol, heptanol, nonanol, decanol, lauryl alcohol, myristyl alcohol, cetyl alcohol, stearyl alcohol and p-tert-benzyl alcohol, di-alcohols such as ethylene glycol, butanediol, hexanediol, nonanediol and tetramethylene glycol, polyhydric-alcohols such as glycerol, sorbitol, xylitol, ribitol and erythritol), methyl lactate and ethyl lactate are usable. These aliphatic alcohols are used as the rate of 0.01 - 10 weight% with respect to the total amount of monomers, although there are slight differences depending on the conditions, such as type of alcohol to be used.

[0212]

In the present invention, a ring-opening polymerization reaction temperature is, in consideration of a polymer generating speed and a thermal composition rate of the generated polymer, within a range of 100 - 200°C, preferably 120 - 180°C.

[0213]

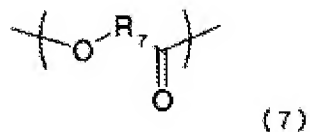
In the present invention, the ring-opening polymerization reaction can be executed under an inert gas atmosphere, such as nitrogen or argon gas, or under reduced or increased pressure, and a catalyst and alcohol may be added gradually at that time.

[0214]

Polyhydroxyalkanoate of the invention is principally constituted of the unit represented by the foregoing chemical formula (1), (5) or (6), but may also be constructed as a copolymer containing a second
5 component, in order to modify physical properties such as mechanical characteristics or decomposition characteristics. For example a unit represented by chemical formula (7) may be further included in the molecule.

10 [0215]

[Chemical Formula 79]



[0216]

wherein R₇ represents a linear or branched alkylene
15 with 1 - 11 carbon atoms, alkyleneoxyalkylene group (each alkylene group being independently with 1 - 2 carbon atoms), a linear or branched alkenyl group with 1 - 11 carbon atoms or an alkylidene group with 1 - 5 carbon atoms which may be substituted with an aryl
20 group; and in case plural units are present, R₇ has the aforementioned meanings independently for each unit.

The second component can specifically be the copolymerization of lactones such as a cyclic diester of α -hydroxycarboxylic acid or an intramolecular ring-

closing compound of ω -hydroxycarboxylic acid.
Specific examples of cyclic diester of α -hydroxycarboxylic acid include intermolecular cyclic diester such as glycolide, lactide, α -hydroxybutyric acid, α -hydroxyisobutyric acid, α -hydroxyvaleric acid, α -hydroxyisovaleric acid, α -hydroxy- α -methylbutyric acid, α -hydroxycaproic acid, α -hydroxyisocaproic acid, α -hydroxy- β -methylvaleric acid, α -hydroxyheptanoic acid, mandelic acid and β -phenyllactic acid. Also in case of presence of an asymmetric carbon, there may be employed an L-isomer, a D-isomer, a racemic body or a meso-form thereof. There is no problem at all that the cyclic diester is formed by different α -oxo acid moleculars. Specifically, it is a cyclic diester between glycolic acid and lactic acid, such as 3-methyl-2, 5-diketo-1, 4-dioxane. Specific examples of lactone, which is an intramolecular ring-closing compound of ω -hydroxycarboxylic acid, include intramolecular ring-closing compounds such as β -propiolactone, β -butyrolactone, β -isovalerolactone, β -caprolactone, β -isocaprolactone, β -methyl- β -valerolactone, γ -butyrolactone, γ -valerolactone, δ -valerolactone, δ -caprolactone, lactone 11-oxydecanoate, p-dioxane and 1,5-dioxebane-2-one, but such examples are not restrictive.

[0217]

A number-averaged molecular weight of

polyhydroxyalkanoate obtained by the polymerization can have various values depending on conditions such as a type or amount of a polymerization catalyst, polymerization temperature and polymerization time, but
5 is preferably 1,000 - 1,000,000.

[0218]

The molecular weight of polyhydroxyalkanoate of the invention can be measured as a relative molecular weight or an absolute molecular weight. In a simpler
10 method, it can be measured for example by GPC (gel permeation chromatography). In a GPC measurement, polyhydroxyalkanoate is dissolved in a solvent and subjected to a measurement in a moving phase. A detector such as a differential refractive index
15 detector (RI) or an ultraviolet detector (UV) can be employed according to the polyhydroxyalkanoate to be measured. The molecular weight is obtained as a relative value in a comparison with a sample (polystyrene or polymethyl methacrylate). The solvent
20 can be selected from those capable of dissolving the polymer, such as dimethylformamide (DMF), dimethyl sulfoxide (DMSO), chloroform, tetrahydrofuran (THF), toluene or hexafluoroisopropanol (HFIP). In case of a polar solvent, the measurement can also be executed by
25 a salt addition.

[0219]

In the present invention, it is preferable to use

the polyhydroxyalkanoate which has a ratio (M_w/M_n) of the weight-averaged molecular weight (M_w) and the number-averaged molecular weight (M_n) measured as mentioned above within a range of 1 - 10.

5 [0220]

In the chemical reaction of the invention, a reaction solvent, a reaction temperature, a reaction time, a purification method and the like are not limited to those described in the foregoing.

10 [Examples]

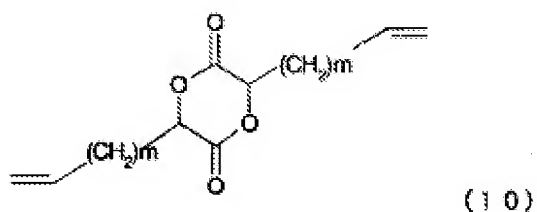
[0221]

In the following, the present invention will be clarified further by examples, but the present invention is not limited to such examples.

15 (Example 1)

[0222]

[Chemical Formula 80]



[0223]

20 wherein m represents an integer selected from 2 - 8.

[Synthesis of 3,6-di(3-butenyl)-1,4-dioxane-2,5-dione represented by chemical formula (10) wherein $m = 2$ from 2-hydroxy-5-hexene acid]

3.0 g of 2-hydroxy-5-hexene acid, 400 ml of

toluene solution and 30 mg of p-toluenesulfonic acid were added in a flask of 1 L equipped with reflux condenser Dean-Stark trap and refluxed under a nitrogen atmosphere. Water accumulated in the trap was removed
5 as needed. The flask was cooled after refluxing for 72 hours. After cleaning with 10 ml of saturated sodium hydrogencarbonate twice, a crude product thus obtained was distilled under a reduced pressure in the presence of zinc oxide to obtain 1.06 g of the targeted 3,6-
10 di(ω' -butenyl)-1,4-dioxane-2,5-dione (yield: 41%). An NMR analysis was conducted under following conditions for specifying the structure of the obtained compound.

<Measuring instrument> FT-NMR: Bruker DPX400
resonance frequency: ^1H = 400 MHz
15 <Measuring condition>
measured species: ^1H
solvent: DMSO- d_6
temperature: room temperature

As a result, the obtained compound was confirmed
20 as the targeted 3,6-di(3-butenyl)-1,4-dioxane-2,5-dione.

[0224]

(Example 2)

Synthesis of 3,6-di(4-pentenyl)-1,4-dioxane-2,5-
25 dione represented by chemical formula (10) wherein m = 3 from 2-hydroxy-6-heptenoic acid

A process was conducted in the same manner as in

Example 1 except for employing 2-hydroxy-6-heptenoic acid instead of 2-hydroxy-5-hexenoic acid, to obtain 1.10 g of 3,6-di(4-pentenyl)-1,4-dioxane-2,5-dione (yield: 42%). An NMR analysis conducted under conditions same as in Example 1 for specifying the structure of the obtained compound confirmed as the targeted 3,6-di(ω' -pentenyl)-1,4-dioxane-2,5-dione. [0225]

(Example 3)

10 Synthesis of 3,6-di(5-hexenyl)-1,4-dioxane-2,5-dione represented by chemical formula (10) wherein m = 4 from 2-hydroxy-7-octenoic acid

A process was conducted in the same manner as in Example 1 except for employing 2-hydroxy-7-octenoic acid instead of 2-hydroxy-5-hexenoic acid, to obtain 1.05 g of 3,6-di(5-hexenyl)-1,4-dioxane-2,5-dione (yield: 40%). An NMR analysis conducted under conditions same as in Example 1 for specifying the structure of the obtained compound confirmed as the targeted 3,6-di(5-hexenyl)-1,4-dioxane-2,5-dione. [0226]

(Example 4)

25 Synthesis of 3,6-di(6-heptenyl)-1,4-dioxane-2,5-dione represented by chemical formula (10) wherein m = 4 from 2-hydroxy-8-nonenic acid

A process was conducted in the same manner as in Example 1 except for employing 2-hydroxy-8-nonenic

acid instead of 2-hydroxy-5-hexene acid, to obtain
1.07 g of 3,6-di(ω' -heptenyl)-1,4-dioxane-2,5-dione
(yield: 40%). An NMR analysis conducted under
conditions same as in Example 1 for specifying the
5 structure of the obtained compound confirmed as the
targeted 3,6-di(6-heptenyl)-1,4-dioxane-2,5-dione.
[0227]

(Example 5)

Synthesis of 3,6-di(2-propenyl)-1,4-dioxane-2,5-
10 dione represented by chemical formula (10) wherein m =
1 from 2-hydroxy-4-pentene acid

A process was conducted in the same manner as in
Example 1 except for employing 2-hydroxy-4-pentene
acid instead of 2-hydroxy-5-hexene acid, to obtain
15 1.09 g of 3,6-di(ω' -propenyl)-1,4-dioxane-2,5-dione
(yield: 43%). An NMR analysis conducted under
conditions same as in Example 1 for specifying the
structure of the obtained compound confirmed as the
targeted 3,6-di(2-propenyl)-1,4-dioxane-2,5-dione.
20 [0228]

(Example 6)

[Polyester synthesis utilizing 3,6-di(3-butenyl)-
1,4-dioxane-2,5-dione]

1.12 g (5.0 mmol) of 3,6-di(3-butenyl)-1,4-
25 dioxane-2,5-dione, 2 ml of a 0.01M toluene solution of
tin octylate (tin 2-ethylhexanoate) and 2 ml of a 0.01M
toluene solution of p-tert-butylbenzyl alcohol were

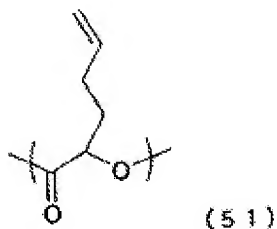
charged in a polymerization ampoule, then subjected to
a drying for 1 hour under a reduced pressure and a
nitrogen replacement, and the ampoule was sealed by
fusing under a reduced pressure and heated at 150°C to
5 execute a ring-opening polymerization. The reaction
was terminated after 1 hour and the mixture was cooled.
An obtained polymer was dissolved in chloroform, and
was re-precipitated in methanol of a 10 times amount of
that of chloroform required for dissolving. The
10 precipitate was recovered and dried under a reduced
pressure to obtain 0.95 g of a polymer. An NMR
analysis was conducted under following conditions for
specifying the structure of the obtained polymer.

<Measuring instrument> FT-NMR: Bruker DPX400
15 resonance frequency: ^1H = 400 MHz
<Measuring condition>
measured species: ^1H
solvent: TMS/ CDCl_3
temperature: room temperature

20 As a result, the obtained polymer was confirmed as
a polyhydroxyalkanoate comprised of a unit represented
by following chemical formula (51):

[0229]

[Chemical Formula 81]



[0230]

An average molecular weight of the obtained polyhydroxyalkanoate was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-GEL Super HM-H, solvent: chloroform, converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 16,500$ and a weight-averaged molecular weight $M_w = 20,000$.

10 [0231]

(Example 7)

[Polyester synthesis utilizing 3,6-di(3-butenyl)-1,4-dioxane-2,5-dione and L-lactide]

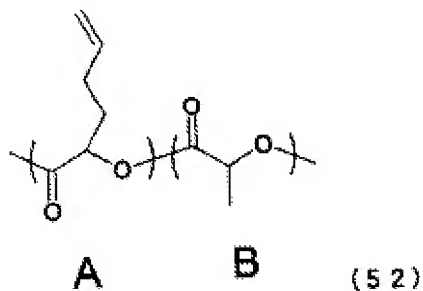
0.11 g (0.5 mmol) of 3,6-di(3-butenyl)-1,4-dioxane-2,5-dione, 0.65 g (4.5 mmol) of L-lactide, 2 ml of a 0.01M toluene solution of tin octylate (tin 2-ethylhexanoate) and 2 ml of a 0.01M toluene solution of p-tert-butylbenzyl alcohol were charged in a polymerization ampoule, then subjected to a drying for 1 hour under a reduced pressure and a nitrogen replacement, and the ampoule was sealed by fusing under a reduced pressure and heated at 150°C to execute a ring-opening polymerization. The reaction was

15
20

terminated after 1 hour and the mixture was cooled. An
obtained polymer was dissolved in chloroform, and was
re-precipitated in methanol of a 10 times amount of
that of chloroform required for dissolving. The
5 precipitate was recovered and dried under a reduced
pressure to obtain 0.63 g of a polymer. An NMR
analysis conducted under conditions same as in Example
6 for specifying the structure of the obtained polymer
confirmed as a polyhydroxyalkanoate copolymer
10 containing a unit represented by below chemical formula
(52) as the monomer unit. It was also confirmed that a
proportion of the monomer units was unit A by 9 mol%
and unit B by 91 mol%.

[0232]

15 [Chemical Formula 82]



[0233]

An average molecular weight of the obtained
polyhydroxyalkanoate was evaluated by gel permeation
20 chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-
GEL Super HM-H, solvent: chloroform, converted as
polystyrene). As a result, there were obtained a

number-averaged molecular weight $M_n = 18,200$ and a weight-averaged molecular weight $M_w = 24,000$.

[0234]

(Example 8)

5 [Polyester synthesis utilizing 3,6-di(4-pentenyl)-1,4-dioxane-2,5-dione and L-lactide]

0.13 g (0.5 mmol) of 3,6-di(4-pentenyl)-1,4-dioxane-2,5-dione, 0.65 g (4.5 mmol) of L-lactide, 2 ml of a 0.1M toluene solution of tin octylate (tin 2-ethylhexanoate) and 2 ml of a 0.1M toluene solution of p-tert-butylbenzyl alcohol were charged in a polymerization ampoule, then subjected to a drying for 1 hour under a reduced pressure and a nitrogen replacement, and the ampoule was sealed by fusing under
10 a reduced pressure and heated at 150°C to execute a ring-opening polymerization. The reaction was terminated after 1 hour and the mixture was cooled. An obtained polymer was dissolved in chloroform, and was re-precipitated in methanol of a 10 times amount of
15 that of chloroform required for dissolving. The precipitate was recovered and dried under a reduced pressure to obtain 0.66 g of a polymer.

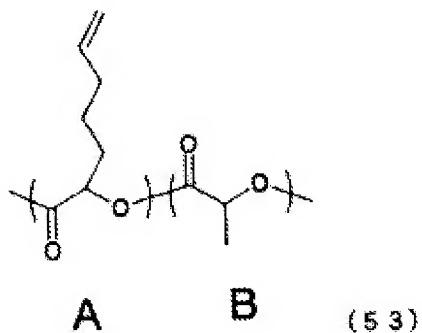
[0235]

An NMR analysis conducted under conditions same as
25 in Example 6 for specifying the structure of the obtained polymer confirmed as a polyhydroxyalkanoate copolymer containing a unit represented by below

chemical formula (53) as the monomer unit. It was also confirmed that a proportion of the monomer units was unit A by 9 mol% and unit B by 91 mol%.

[0236]

5 [Chemical Formula 83]



[0237]

An average molecular weight of the obtained polyhydroxyalkanoate was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-GEL Super HM-H, solvent: chloroform, converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 17,800$ and a weight-averaged molecular weight $M_w = 24,200$.

15 [0238]

(Example 9)

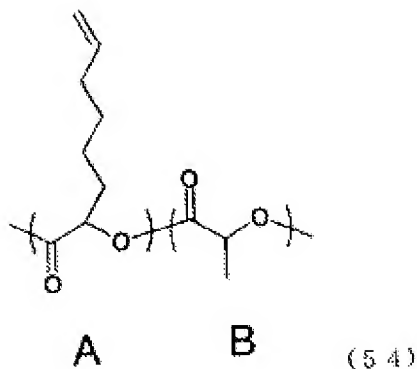
[Polyester synthesis utilizing 3,6-di(5-hexenyl)-1,4-dioxane-2,5-dione and L-lactide]

0.14 g (0.5 mmol) of 3,6-di(5-hexenyl)-1,4-dioxane-2,5-dione, 0.65 g (4.5 mmol) of L-lactide, 2 ml of a 0.01M toluene solution of tin octylate (tin 2-ethylhexanoate) and 2 ml of a 0.01M toluene solution of

p-tert-butylbenzyl alcohol were charged in a polymerization ampoule, then subjected to a drying for 1 hour under a reduced pressure and a nitrogen replacement, and the ampoule was sealed by fusing under a reduced pressure and heated at 150°C to execute a ring-opening polymerization. The reaction was terminated after 1 hour and the mixture was cooled. An obtained polymer was dissolved in chloroform, and was re-precipitated in methanol of a 10 times amount of that of chloroform required for dissolving. The precipitate was recovered and dried under a reduced pressure to obtain 0.62 g of a polymer. An NMR analysis conducted under conditions same as in Example 6 for specifying the structure of the obtained polymer confirmed as a polyhydroxyalkanoate copolymer containing a unit represented by below chemical formula (54) as the monomer unit. It was also confirmed that a proportion of the monomer units was unit A by 8 mol% and unit B by 92 mol%.

[0239]

[Chemical Formula 84]



[0240]

An average molecular weight of the obtained polyhydroxyalkanoate was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-GEL Super HM-H, solvent: chloroform, converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 16,500$ and a weight-averaged molecular weight $M_w = 21,900$.

10 [0241]

(Example 10)

[Polyester synthesis utilizing 3,6-di(6-heptenyl)-1,4-dioxane-2,5-dione and L-lactide]

0.15 g (0.5 mmol) of 3,6-di(6-heptenyl)-1,4-dioxane-2,5-dione, 0.65 g (4.5 mmol) of L-lactide, 2 ml of a 0.01M toluene solution of tin octylate (tin 2-ethylhexanoate) and 2 ml of a 0.01M toluene solution of p-tert-butylbenzyl alcohol were charged in a polymerization ampoule, then subjected to a drying for 1 hour under a reduced pressure and a nitrogen replacement, and the ampoule was sealed by fusing under

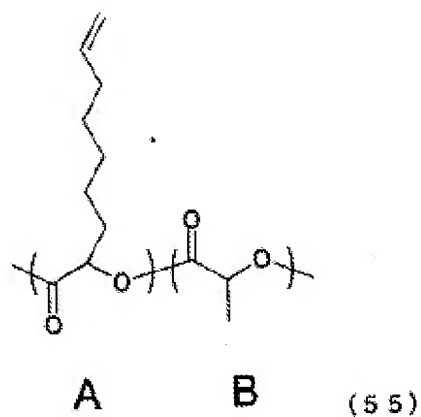
15

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a reduced pressure and heated at 150°C to execute a ring-opening polymerization. The reaction was terminated after 1 hour and the mixture was cooled. An obtained polymer was dissolved in chloroform, and was re-precipitated in methanol of a 10 times amount of that of chloroform required for dissolving. The precipitate was recovered and dried under a reduced pressure to obtain 0.64 g of a polymer. An NMR analysis conducted under conditions same as in Example 6 for specifying the structure of the obtained polymer confirmed as a polyhydroxyalkanoate copolymer containing a unit represented by below chemical formula (55) as the monomer unit. It was also confirmed that a proportion of the monomer units was unit A by 7 mol% and unit B by 93 mol%.

[0242]

[Chemical Formula 85]



[0243]

20 An average molecular weight of the obtained

polyhydroxyalkanoate was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-GEL Super HM-H, solvent: chloroform, converted as polystyrene). As a result, there were obtained a
5 number-averaged molecular weight $M_n = 15,700$ and a weight-averaged molecular weight $M_w = 21,800$.

[0244]

(Example 11)

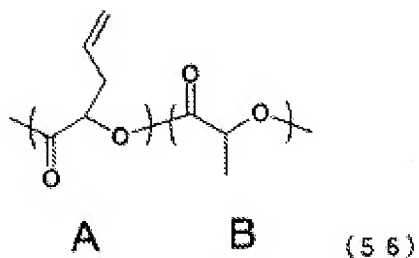
[Polyester synthesis utilizing 3,6-di(2-propenyl)-
10 1,4-dioxane-2,5-dione and L-lactide]

0.10 g (0.5 mmol) of 3,6-di(2-propenyl)-1,4-dioxane-2,5-dione, 0.65 g (4.5 mmol) of L-lactide, 2 ml of a 0.01M toluene solution of tin octylate (tin 2-ethylhexanoate) and 2 ml of a 0.01M toluene solution of
15 p-tert-butylbenzyl alcohol were charged in a polymerization ampoule, then subjected to a drying for 1 hour under a reduced pressure and a nitrogen replacement, and the ampoule was sealed by fusing under a reduced pressure and heated at 150°C to execute a
20 ring-opening polymerization. The reaction was terminated after 1 hour and the mixture was cooled. An obtained polymer was dissolved in chloroform, and was re-precipitated in methanol of a 10 times amount of that of chloroform required for dissolving. The
25 precipitate was recovered and dried under a reduced pressure to obtain 0.65 g of a polymer. An NMR analysis conducted under conditions same as in Example

6 for specifying the structure of the obtained polymer
confirmed as a polyhydroxyalkanoate copolymer
containing a unit represented by below chemical formula
(56) as the monomer unit. It was also confirmed that a
5 proportion of the monomer units was unit A by 9 mol%
and unit B by 91 mol%.

[0245]

[Chemical Formula 86]



10 [0246]

An average molecular weight of the obtained
polyhydroxyalkanoate was evaluated by gel permeation
chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-
GEL Super HM-H, solvent: chloroform, converted as
15 polystyrene). As a result, there were obtained a
number-averaged molecular weight $M_n = 17,200$ and a
weight-averaged molecular weight $M_w = 22,500$.

[0247]

(Example 12)

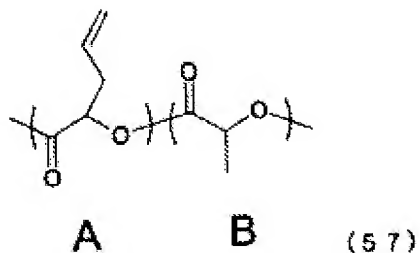
20 [Polyester synthesis utilizing 3,6-di(2-propenyl)-
1,4-dioxane-2,5-dione and L-lactide]

0.98 g (5.0 mmol) of 3,6-di(2-propenyl)-1,4-
dioxane-2,5-dione, 6.49 g (45.0 mmol) of L-lactide, 20

ml of a 0.01M toluene solution of tin octylate (tin 2-ethylhexanoate) and 20 ml of a 0.01M toluene solution of p-tert-butylbenzyl alcohol were charged in a polymerization ampoule, then subjected to a drying for 5 2 hours under a reduced pressure and a nitrogen replacement, and the ampoule was sealed by fusing under a reduced pressure and heated at 150°C to execute a ring-opening polymerization. The reaction was terminated after 1 hour and the mixture was cooled. An 10 obtained polymer was dissolved in chloroform, and was re-precipitated in methanol of a 10 times amount of that of chloroform required for dissolving. The precipitate was recovered and dried under a reduced pressure to obtain 6.55 g of a polymer. An NMR 15 analysis conducted under conditions same as in Example 6 for specifying the structure of the obtained polymer confirmed as a polyhydroxyalkanoate copolymer containing a unit represented by below chemical formula (57) as the monomer unit. It was also confirmed that a 20 proportion of the monomer units was unit A by 9 mol% and unit B by 91 mol%.

[0248]

[Chemical Formula 87]



[0249]

An average molecular weight of the obtained polyhydroxyalkanoate was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-GEL Super HM-H, solvent: chloroform, converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 17,400$ and a weight-averaged molecular weight $M_w = 23,300$.

10 [0250]

(Example 13)

[Polyester synthesis utilizing 3,6-di(2-propenyl)-1,4-dioxane-2,5-dione and L-lactide]

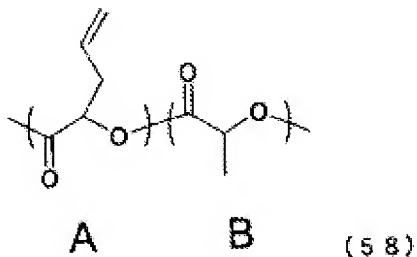
0.49 g (0.25 mmol) of 3,6-di(2-propenyl)-1,4-dioxane-2,5-dione, 0.68 g (4.75 mmol) of L-lactide, 2 ml of a 0.01M toluene solution of tin octylate (tin 2-ethylhexanoate) and 2 ml of a 0.01M toluene solution of p-tert-butylbenzyl alcohol were charged in a polymerization ampoule, then subjected to a drying for 1 hour under a reduced pressure and a nitrogen replacement, and the ampoule was sealed by fusing under a reduced pressure and heated at 150°C to execute a ring-opening polymerization. The reaction was

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terminated after 1 hour and the mixture was cooled. An
obtained polymer was dissolved in chloroform, and was
re-precipitated in methanol of a 10 times amount of
that of chloroform required for dissolving. The
5 precipitate was recovered and dried under a reduced
pressure to obtain 0.64 g of a polymer. An NMR
analysis conducted under conditions same as in Example
6 for specifying the structure of the obtained polymer
confirmed as a polyhydroxyalkanoate copolymer
10 containing a unit represented by below chemical formula
(58) as the monomer unit. It was also confirmed that a
proportion of the monomer units was unit A by 4 mol%
and unit B by 96 mol%.

[0251]

15 [Chemical Formula 88]



[0252]

An average molecular weight of the obtained
polyhydroxyalkanoate was evaluated by gel permeation
20 chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-
GEL Super HM-H, solvent: chloroform, converted as
polystyrene). As a result, there were obtained a

number-averaged molecular weight $M_n = 18,000$ and a weight-averaged molecular weight $M_w = 22,500$.

[0253]

(Example 14)

5 [Polyester synthesis utilizing 3,6-di(2-propenyl)-1,4-dioxane-2,5-dione and L-lactide]

0.15 g (0.75 mmol) of 3,6-di(2-propenyl)-1,4-dioxane-2,5-dione, 0.61 g (4.25 mmol) of L-lactide, 2 ml of a 0.01M toluene solution of tin octylate (tin 2-ethylhexanoate) and 2 ml of a 0.01M toluene solution of p-tert-butylbenzyl alcohol were charged in a polymerization ampoule, then subjected to a drying for 1 hour under a reduced pressure and a nitrogen replacement, and the ampoule was sealed by fusing under a reduced pressure and heated at 150°C to execute a ring-opening polymerization. The reaction was terminated after 1 hour and the mixture was cooled. An obtained polymer was dissolved in chloroform, and was re-precipitated in methanol of a 10 times amount of that of chloroform required for dissolving. The precipitate was recovered and dried under a reduced pressure to obtain 0.64 g of a polymer. An NMR analysis conducted under conditions same as in Example 6 for specifying the structure of the obtained polymer confirmed as a polyhydroxyalkanoate copolymer containing a unit represented by below chemical formula (59) as the monomer unit. It was also confirmed that a

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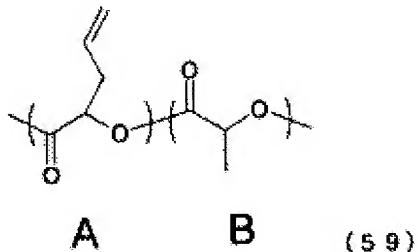
20

25

proportion of the monomer units was unit A by 14 mol% and unit B by 86 mol%.

[0254]

[Chemical Formula 89]



5

[0255]

An average molecular weight of the obtained polyhydroxyalkanoate was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-
10 GEL Super HM-H, solvent: chloroform, converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 15,800$ and a weight-averaged molecular weight $M_w = 19,900$.

[0256]

15

(Example 15)

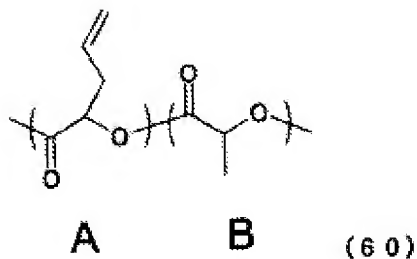
[Polyester synthesis utilizing 3,6-di(2-propenyl)-1,4-dioxane-2,5-dione and L-lactide]

0.20 g (1.0 mmol) of 3,6-di(2-propenyl)-1,4-dioxane-2,5-dione, 0.58 g (4.0 mmol) of L-lactide, 2 ml
20 of a 0.01M toluene solution of tin octylate (tin 2-ethylhexanoate) and 2 ml of a 0.01M toluene solution of p-tert-butylbenzyl alcohol were charged in a polymerization ampoule, then subjected to a drying for

1 hour under a reduced pressure and a nitrogen replacement, and the ampoule was sealed by fusing under a reduced pressure and heated at 150°C to execute a ring-opening polymerization. The reaction was
5 terminated after 1 hour and the mixture was cooled. An obtained polymer was dissolved in chloroform, and was re-precipitated in methanol of a 10 times amount of that of chloroform required for dissolving. The precipitate was recovered and dried under a reduced
10 pressure to obtain 0.62 g of a polymer. An NMR analysis conducted under conditions same as in Example 6 for specifying the structure of the obtained polymer confirmed as a polyhydroxyalkanoate copolymer containing a unit represented by below chemical formula
15 (60) as the monomer unit. It was also confirmed that a proportion of the monomer units was unit A by 18 mol% and unit B by 82 mol%.

[0257]

[Chemical Formula 90]



20

[0258]

An average molecular weight of the obtained polyhydroxyalkanoate was evaluated by gel permeation

chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-GEL Super HM-H, solvent: chloroform, converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 14,700$ and a
5 weight-averaged molecular weight $M_w = 18,600$.

[0259]

(Example 16)

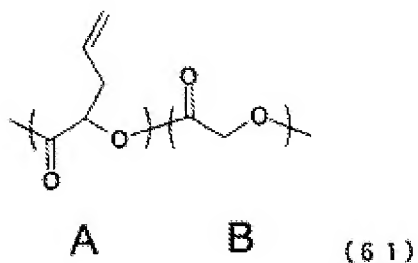
[Polyester synthesis utilizing 3,6-di(2-propenyl)-1,4-dioxane-2,5-dione and glycolide (1,4-dioxane-2,5-
10 dione)]

0.10 g (0.5 mmol) of 3,6-di(2-propenyl)-1,4-dioxane-2,5-dione, 0.52 g (4.5 mmol) of glycolide, 2 ml of a 0.01M toluene solution of tin octylate (tin 2-ethylhexanoate) and 2 ml of a 0.01M toluene solution of
15 p-tert-butylbenzyl alcohol were charged in a polymerization ampoule, then subjected to a drying for 1 hour under a reduced pressure and a nitrogen replacement, and the ampoule was sealed by fusing under a reduced pressure and heated at 150°C to execute a
20 ring-opening polymerization. The reaction was terminated after 1 hour and the mixture was cooled. An obtained polymer was dissolved in chloroform, and was re-precipitated in methanol of a 10 times amount of that of chloroform required for dissolving. The
25 precipitate was recovered and dried under a reduced pressure to obtain 0.53 g of a polymer. An NMR analysis conducted under conditions same as in Example

6 for specifying the structure of the obtained polymer
confirmed as a polyhydroxyalkanoate copolymer
containing a unit represented by below chemical formula
(61) as the monomer unit. It was also confirmed that a
5 proportion of the monomer units was unit A by 10 mol%
and unit B by 90 mol%.

[0260]

[Chemical Formula 91]



10 [0261]

An average molecular weight of the obtained
polyhydroxyalkanoate was evaluated by gel permeation
chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-
GEL Super HM-H, solvent: chloroform, converted as
15 polystyrene). As a result, there were obtained a
number-averaged molecular weight $M_n = 18,500$ and a
weight-averaged molecular weight $M_w = 24,200$.

[0262]

(Example 17)

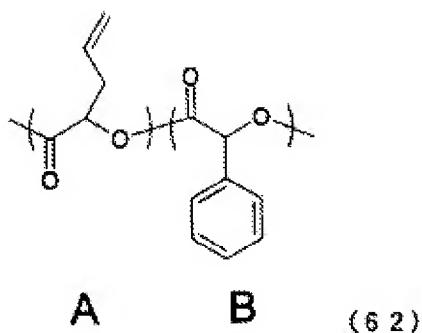
20 [Polyester synthesis utilizing 3,6-di(2-propenyl)-
1,4-dioxane-2,5-dione and mandelide (3,6-diphenyl-1,4-
dioxane-2,5-dione)]

0.10 g (0.5 mmol) of 3,6-di(2-propenyl)-1,4-

dioxane-2,5-dione, 1.21 g (4.5 mmol) of mandelide, 2 ml of a 0.01M toluene solution of tin octylate (tin 2-ethylhexanoate) and 2 ml of a 0.01M toluene solution of p-tert-butylbenzyl alcohol were charged in a
5 polymerization ampoule, then subjected to a drying for 1 hour under a reduced pressure and a nitrogen replacement, and the ampoule was sealed by fusing under a reduced pressure and heated at 150°C to execute a ring-opening polymerization. The reaction was
10 terminated after 1 hour and the mixture was cooled. An obtained polymer was dissolved in chloroform, and was re-precipitated in methanol of a 10 times amount of that of chloroform required for dissolving. The precipitate was recovered and dried under a reduced
15 pressure to obtain 1.05 g of a polymer. An NMR analysis conducted under conditions same as in Example 6 for specifying the structure of the obtained polymer confirmed as a polyhydroxyalkanoate copolymer containing a unit represented by below chemical formula
20 (62) as the monomer unit. It was also confirmed that a proportion of the monomer units was unit A by 8 mol% and unit B by 92 mol%.

[0263]

[Chemical Formula 92]



[0264]

An average molecular weight of the obtained polyhydroxyalkanoate was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-GEL Super HM-H, solvent: chloroform, converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 17,000$ and a weight-averaged molecular weight $M_w = 31,500$.

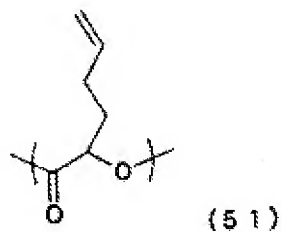
10 [0265]

(Example 18)

Oxidation reaction of a polyhydroxyalkanoate constituted of a unit represented by chemical formula (51) synthesized in Example 6

15 [0266]

[Chemical Formula 93]



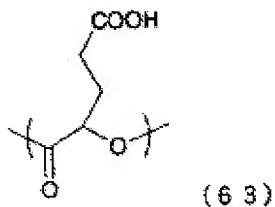
[0267]

0.50 g of polyhydroxyalkanoate obtained in Example 6 and constituted of a unit represented by chemical formula (51) were placed in an eggplant-shaped flask, and dissolved by adding 30 ml of acetone. The solution
5 was placed in an ice bath and agitated while added 5 ml of acetic acid and 3.54 g of 18-crown-6-ether. Then 2.82 g of potassium permanganate was slowly added in the ice bath and the mixture was agitated for 2 hours in the ice bath and further 18 hours at the room
10 temperature. After the reaction, 60 ml of ethyl acetate and further 45 ml of water were added. Next, sodium hydrogen sulfite was added until overacidity was removed. Then, the liquid factor was made to pH = 1 by 1.0 N of hydrochloric acid. The organic layer was
15 separated. The organic layer was recovered and washed three times with 1.0 N of hydrochloric acid. After recovering the organic layer, the solvent was distilled off to recover a crude polymer. Next, the polymer was recovered after cleaning with 50 ml of water and 50 ml
20 of methanol, and then cleaning three times with 50 ml of water. It was then dissolved in THF, and was re-precipitated in methanol of a 50-times amount of that of THF required for dissolving. The precipitate was recovered and dried under a reduced pressure to obtain
25 0.48 g of polymer. An NMR analysis conducted under conditions same as in Example 6 for specifying the structure of the obtained polymer confirmed a

polyhydroxyalkanoate containing units represented by
chemical formula (63) as monomer units.

[0268]

[Chemical Formula 94]



5

[0269]

An average molecular weight of the obtained
polyhydroxyalkanoate was evaluated by gel permeation
chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-
10 GEL Super HM-H, solvent: chloroform, converted as
polystyrene). As a result, there were obtained a
number-averaged molecular weight $M_n = 12,400$ and a
weight-averaged molecular weight $M_w = 16,200$.

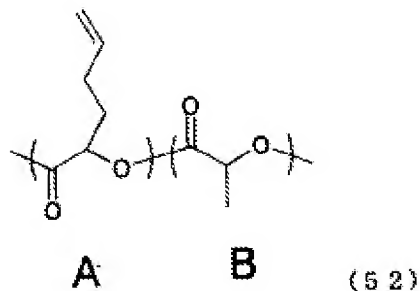
[0270]

15 (Example 19)

Oxidation reaction of a polyhydroxyalkanoate
constituted of a unit represented by chemical formula
(52) synthesized in Example 7

[0271]

20 [Chemical Formula 95]



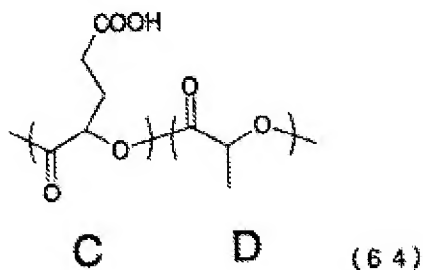
[0272]

0.50 g of polyhydroxyalkanoate copolymer (A: 9 mol%, B: 91 mol%) obtained in Example 7 and constituted of a unit represented by chemical formula (52) were placed in an eggplant-shaped flask, and dissolved by adding 30 ml of acetone. The solution was placed in an ice bath and agitated while added 5 ml of acetic acid and 0.47 g of 18-crown-6-ether. Then 0.38 g of potassium permanganate was slowly added in the ice bath and the mixture was agitated for 2 hours in the ice bath and further 18 hours at the room temperature. After the reaction, 60 ml of ethyl acetate and further 45 ml of water were added. Next, sodium hydrogen sulfite was added until overacidity was removed. Then, the liquid factor was made to pH = 1 by 1.0 N of hydrochloric acid. The organic layer was separated. The organic layer was recovered and washed three times with 1.0 N of hydrochloric acid. After recovering the organic layer, the solvent was distilled off to recover a crude polymer. Next, the polymer was recovered after cleaning with 50 ml of water and 50 ml of methanol, and

then cleaning three times with 50 ml of water. It was then dissolved in 3 ml of THF, and was re-precipitated in methanol of a 50-times amount of that of THF required for dissolving. The precipitate was recovered and dried under a reduced pressure to obtain 0.44 g of polymer. An NMR analysis conducted under conditions same as in Example 6 for specifying the structure of the obtained polymer confirmed a polyhydroxyalkanoate containing units represented by chemical formula (64) as monomer units.

[0273]

[Chemical Formula 96]



[0274]

An average molecular weight of the obtained polyhydroxyalkanoate was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-GEL Super HM-H, solvent: chloroform, converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 13,200$ and a weight-averaged molecular weight $M_w = 18,200$.

[0275]

Furthermore, in order to calculate the units of

the obtained polyhydroxyalkanoate, the calculation was made by methyl esterification of the carboxyl group at the end of the side chain of the polyhydroxyalkanoate using trimethylsilyl diazomethane. 30 mg of the
5 targeted polyhydroxyalkanoate were placed in a 100-ml eggplant-shaped flask and dissolved by adding 2.1 ml of chloroform and 0.7 ml of methanol. Then 0.5 ml of a 2 mol/L hexane solution of trimethylsilyl diazomethane were added and the mixture was agitated for 1 hour at
10 the room temperature. After the reaction, the solvent was distilled off to recover the polymer. The polymer was washed with 50 ml of methanol, then recovered, and dried under a reduced pressure to obtain 31 mg of polyhydroxyalkanoate.

15 [0276]

An NMR analysis conducted under conditions same as in Example 6 confirmed that a proportion of the units of the polyhydroxyalkanoate represented by chemical formula (64) was a copolymer as unit C by 8 mol% and
20 unit D by 92 mol%.

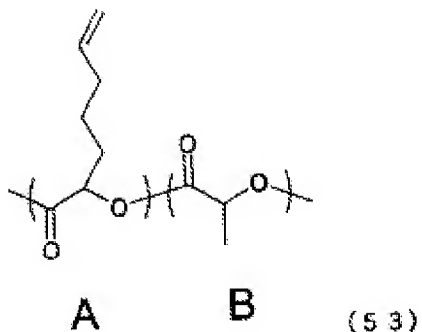
[0277]

(Example 20)

Oxidation reaction of a polyhydroxyalkanoate constituted of a unit represented by chemical formula
25 (53) synthesized in Example 8

[0278]

[Chemical Formula 97]



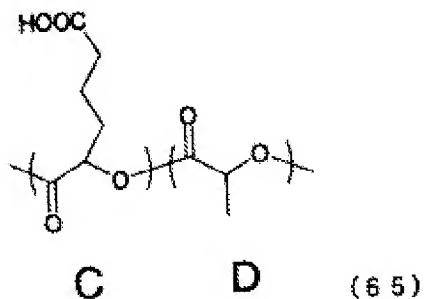
[0279]

0.50 g of polyhydroxyalkanoate copolymer (A: 9 mol%, B: 91 mol%) obtained in Example 8 and constituted of a unit represented by chemical formula (53) were placed in an eggplant-shaped flask, and dissolved by adding 30 ml of acetone. The solution was placed in an ice bath and agitated while added 5 ml of acetic acid and 0.46 g of 18-crown-6-ether. Then 0.37 g of potassium permanganate was slowly added in the ice bath and the mixture was agitated for 2 hours in the ice bath and further 18 hours at the room temperature. After the reaction, 60 ml of ethyl acetate and further 45 ml of water were added. Next, sodium hydrogen sulfite was added until overacidity was removed. Then, the liquid factor was made to pH = 1 by 1.0 N of hydrochloric acid. The organic layer was separated. The organic layer was recovered and washed three times with 1.0 N of hydrochloric acid. After recovering the organic layer, the solvent was distilled off to recover a crude polymer. Next, the polymer was recovered after

cleaning with 50 ml of water and 50 ml of methanol, and then cleaning three times with 50 ml of water. It was then dissolved in THF, and was re-precipitated in methanol of a 50-times amount of that of THF required
5 for dissolving. The precipitate was recovered and dried under a reduced pressure to obtain 0.42 g of polymer. An NMR analysis conducted under conditions same as in Example 6 for specifying the structure of the obtained polymer confirmed a polyhydroxyalkanoate
10 containing units represented by chemical formula (65) as monomer units.

[0280]

[Chemical Formula 98]



15 [0281]

An average molecular weight of the obtained polyhydroxyalkanoate was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-GEL Super HM-H, solvent: chloroform, converted as
20 polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 13,000$ and a weight-averaged molecular weight $M_w = 18,100$.

Furthermore, in order to calculate the units of the obtained polyhydroxyalkanoate, the calculation was made by methyl esterification of the carboxyl group at the end of the side chain of the polyhydroxyalkanoate using
5 trimethylsilyl diazomethane. 30 mg of the targeted polyhydroxyalkanoate were placed in a 100-ml eggplant-shaped flask and dissolved by adding 2.1 ml of chloroform and 0.7 ml of methanol. Then 0.5 ml of a 2 mol/L hexane solution of trimethylsilyl diazomethane
10 were added and the mixture was agitated for 1 hour at the room temperature. After the reaction, the solvent was distilled off to recover the polymer. The polymer was washed with 50 ml of methanol, then recovered, and dried under a reduced pressure to obtain 29 mg of
15 polyhydroxyalkanoate.

[0282]

An NMR analysis conducted under conditions same as in Example 6 confirmed that a proportion of the units of the polyhydroxyalkanoate represented by chemical
20 formula (65) was a copolymer as unit C by 8 mol% and unit D by 92 mol%.

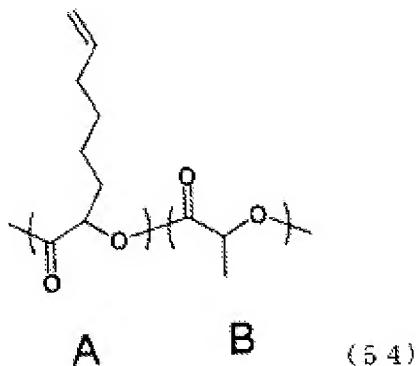
[0283]

(Example 21)

Oxidation reaction of a polyhydroxyalkanoate
25 constituted of a unit represented by chemical formula (54) synthesized in Example 9

[0284]

[Chemical Formula 99]



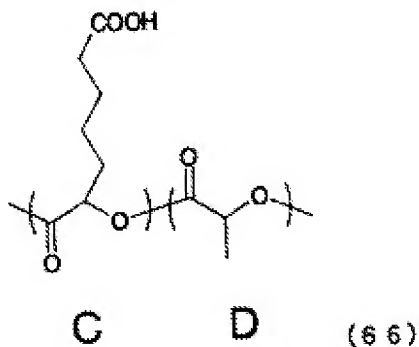
[0285]

0.50 g of polyhydroxyalkanoate copolymer (A: 8
5 mol%, B: 92 mol%) obtained in Example 9 and constituted
of a unit represented by chemical formula (54) were
placed in an eggplant-shaped flask, and dissolved by
adding 30 ml of acetone. The solution was placed in an
ice bath and agitated while added 5 ml of acetic acid
10 and 0.40 g of 18-crown-6-ether. Then 0.32 g of
potassium permanganate was slowly added in the ice bath
and the mixture was agitated for 2 hours in the ice
bath and further 18 hours at the room temperature.
After the reaction, 60 ml of ethyl acetate and further
15 45 ml of water were added. Next, sodium hydrogen
sulfite was added until overacidity was removed. Then,
the liquid factor was made to pH = 1 by 1.0 N of
hydrochloric acid. The organic layer was separated.
The organic layer was recovered and washed three times
20 with 1.0 N of hydrochloric acid. After recovering the

organic layer, the solvent was distilled off to recover
a crude polymer. Next, the polymer was recovered after
cleaning with 50 ml of water and 50 ml of methanol, and
then cleaning three times with 50 ml of water. It was
5 then dissolved in THF, and was re-precipitated in
methanol of a 50-times amount of that of THF required
for dissolving. The precipitate was recovered and
dried under a reduced pressure to obtain 0.44 g of
polymer. An NMR analysis conducted under conditions
10 same as in Example 6 for specifying the structure of
the obtained polymer confirmed a polyhydroxyalkanoate
containing units represented by chemical formula (66)
as monomer units.

[0286]

15 [Chemical Formula 100]



[0287]

An average molecular weight of the obtained
polyhydroxyalkanoate was evaluated by gel permeation
20 chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-
GEL Super HM-H, solvent: chloroform, converted as

polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 11,700$ and a weight-averaged molecular weight $M_w = 16,400$.

Furthermore, in order to calculate the units of the
5 obtained polyhydroxyalkanoate, the calculation was made by methyl esterification of the carboxyl group at the end of the side chain of the polyhydroxyalkanoate using trimethylsilyl diazomethane. 30 mg of the targeted polyhydroxyalkanoate were placed in a 100-ml eggplant-
10 shaped flask and dissolved by adding 2.1 ml of chloroform and 0.7 ml of methanol. Then 0.5 ml of a 2 mol/L hexane solution of trimethylsilyl diazomethane were added and the mixture was agitated for 1 hour at the room temperature. After the reaction, the solvent
15 was distilled off to recover the polymer. The polymer was washed with 50 ml of methanol, then recovered, and dried under a reduced pressure to obtain 28 mg of polyhydroxyalkanoate.

[0288]

20 An NMR analysis conducted under conditions same as in Example 6 confirmed that a proportion of the units of the polyhydroxyalkanoate represented by chemical formula (66) was a copolymer as unit C by 8 mol% and unit D by 92 mol%.

25 [0289]

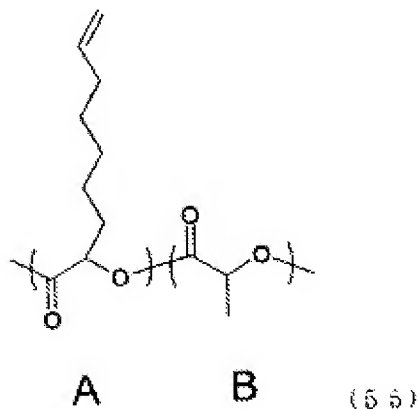
(Example 22)

Oxidation reaction of a polyhydroxyalkanoate

constituted of a unit represented by chemical formula
(55) synthesized in Example 10

[0290]

[Chemical Formula 101]



5

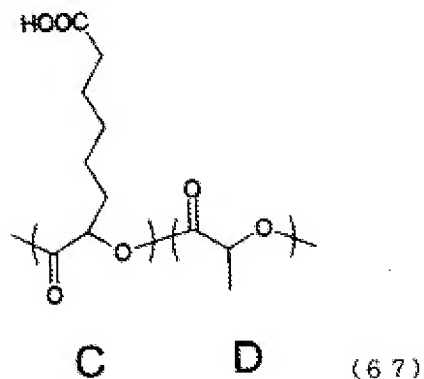
[0291]

0.50 g of polyhydroxyalkanoate copolymer (A: 7
mol%, B: 93 mol%) obtained in Example 8 and constituted
of a unit represented by chemical formula (55) were
10 placed in an eggplant-shaped flask, and dissolved by
adding 30 ml of acetone. The solution was placed in an
ice bath and agitated while added 5 ml of acetic acid
and 0.35 g of 18-crown-6-ether. Then 0.28 g of
potassium permanganate was slowly added in the ice bath
15 and the mixture was agitated for 2 hours in the ice
bath and further 18 hours at the room temperature.
After the reaction, 60 ml of ethyl acetate and further
45 ml of water were added. Next, sodium hydrogen
sulfite was added until overacidity was removed. Then,
20 the liquid factor was made to pH = 1 by 1.0 N of

hydrochloric acid. The organic layer was separated.
The organic layer was recovered and washed three times
with 1.0 N of hydrochloric acid. After recovering the
organic layer, the solvent was distilled off to recover
5 a crude polymer. Next, the polymer was recovered after
cleaning with 50 ml of water and 50 ml of methanol, and
then cleaning three times with 50 ml of water. It was
then dissolved in THF, and was re-precipitated in
methanol of a 50-times amount of that of THF required
10 for dissolving. The precipitate was recovered and
dried under a reduced pressure to obtain 0.42 g of
polymer. An NMR analysis conducted under conditions
same as in Example 6 for specifying the structure of
the obtained polymer confirmed a polyhydroxyalkanoate
15 containing units represented by chemical formula (67)
as monomer units.

[0292]

[Chemical Formula 102]



20 [0293]

An average molecular weight of the obtained polyhydroxyalkanoate was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-GEL Super HM-H, solvent: chloroform, converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 11,400$ and a weight-averaged molecular weight $M_w = 16,300$. Furthermore, in order to calculate the units of the obtained polyhydroxyalkanoate, the calculation was made by methyl esterification of the carboxyl group at the end of the side chain of the polyhydroxyalkanoate using trimethylsilyl diazomethane.

[0294]

30 mg of the targeted polyhydroxyalkanoate were placed in a 100-ml eggplant-shaped flask and dissolved by adding 2.1 ml of chloroform and 0.7 ml of methanol. Then 0.5 ml of a 2 mol/L hexane solution of trimethylsilyl diazomethane were added and the mixture was agitated for 1 hour at the room temperature. After the reaction, the solvent was distilled off to recover the polymer. The polymer was washed with 50 ml of methanol, then recovered, and dried under a reduced pressure to obtain 30 mg of polyhydroxyalkanoate.

[0295]

An NMR analysis conducted under conditions same as in Example 6 confirmed that a proportion of the units of the polyhydroxyalkanoate represented by chemical

formula (67) was a copolymer as unit C by 7 mol% and unit D by 93 mol%.

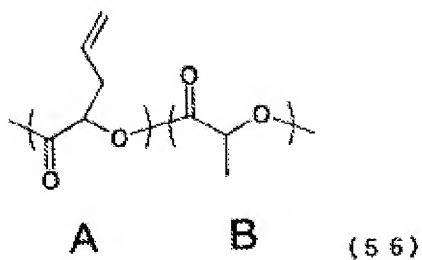
[0296]

(Example 23)

5 Oxidation reaction of a polyhydroxyalkanoate constituted of a unit represented by chemical formula (56) synthesized in Example 11

[0297]

[Chemical Formula 103]



[0298]

0.50 g of polyhydroxyalkanoate copolymer (A: 9 mol%, B: 91 mol%) obtained in Example 11 and constituted of a unit represented by chemical formula (52) were placed in an eggplant-shaped flask, and dissolved by adding 30 ml of acetone. The solution was placed in an ice bath and agitated while added 5 ml of acetic acid and 0.48 g of 18-crown-6-ether. Then 0.38 g of potassium permanganate was slowly added in the ice bath and the mixture was agitated for 2 hours in the ice bath and further 18 hours at the room temperature. After the reaction, 60 ml of ethyl acetate and further 45 ml of water were added. Next, sodium hydrogen

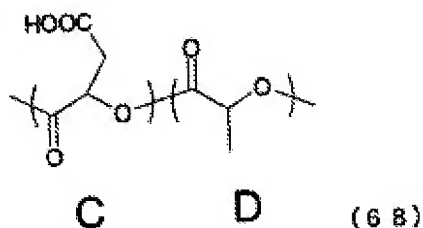
15

20

sulfite was added until overacidity was removed. Then, the liquid factor was made to pH = 1 by 1.0 N of hydrochloric acid. The organic layer was separated. The organic layer was recovered and washed three times
5 with 1.0 N of hydrochloric acid. After recovering the organic layer, the solvent was distilled off to recover a crude polymer. Next, the polymer was recovered after cleaning with 50 ml of water and 50 ml of methanol, and then cleaning three times with 50 ml of water. It was
10 then dissolved in THF, and was re-precipitated in methanol of a 50-times amount of that of THF required for dissolving. The precipitate was recovered and dried under a reduced pressure to obtain 0.45 g of polymer. An NMR analysis conducted under conditions
15 same as in Example 6 for specifying the structure of the obtained polymer confirmed a polyhydroxyalkanoate containing units represented by chemical formula (68) as monomer units.

[0299]

20 [Chemical Formula 104]



[0300]

An average molecular weight of the obtained

polyhydroxyalkanoate was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-GEL Super HM-H, solvent: chloroform, converted as polystyrene). As a result, there were obtained a
5 number-averaged molecular weight $M_n = 12,800$ and a weight-averaged molecular weight $M_w = 17,700$. Furthermore, in order to calculate the units of the obtained polyhydroxyalkanoate, the calculation was made by methyl esterification of the carboxyl group at the
10 end of the side chain of the polyhydroxyalkanoate using trimethylsilyl diazomethane. 30 mg of the targeted polyhydroxyalkanoate were placed in a 100-ml eggplant-shaped flask and dissolved by adding 2.1 ml of chloroform and 0.7 ml of methanol. Then 0.5 ml of a 2
15 mol/L hexane solution of trimethylsilyl diazomethane were added and the mixture was agitated for 1 hour at the room temperature. After the reaction, the solvent was distilled off to recover the polymer. The polymer was washed with 50 ml of methanol, then recovered, and
20 dried under a reduced pressure to obtain 29 mg of polyhydroxyalkanoate.

[0301]

An NMR analysis conducted under conditions same as in Example 6 confirmed that a proportion of the units
25 of the polyhydroxyalkanoate represented by chemical formula (68) was a copolymer as unit C by 8 mol% and unit D by 92 mol%.

[0302]

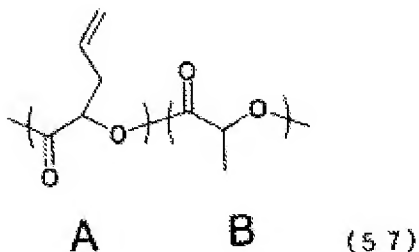
(Example 24)

Oxidation reaction of a polyhydroxyalkanoate constituted of a unit represented by chemical formula

5 (57) synthesized in Example 12

[0303]

[Chemical Formula 105]



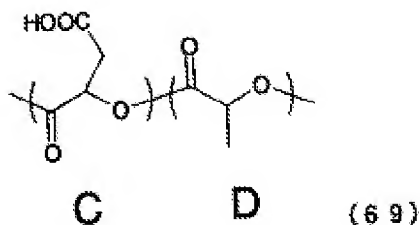
[0304]

10 6.00 g of polyhydroxyalkanoate copolymer (A: 9
mol%, B: 91 mol%) obtained in Example 12 and
constituted of a unit represented by chemical formula
(57) were placed in an eggplant-shaped flask, and
dissolved by adding 360 ml of acetone. The solution
15 was placed in an ice bath and agitated while added 60
ml of acetic acid and 5.75 g of 18-crown-6-ether. Then
4.59 g of potassium permanganate was slowly added in
the ice bath and the mixture was agitated for 2 hours
in the ice bath and further 18 hours at the room
20 temperature. After the reaction, 720 ml of ethyl
acetate and further 540 ml of water were added. Next,
sodium hydrogen sulfite was added until overacidity was
removed. Then, the liquid factor was made to pH = 1 by

1.0 N of hydrochloric acid. The organic layer was separated. The organic layer was recovered and washed three times with 1.0 N of hydrochloric acid. After recovering the organic layer, the solvent was distilled
5 off to recover a crude polymer. Next, the polymer was recovered after cleaning with 600 ml of water and 600 ml of methanol, and then cleaning three times with 600 ml of water. It was then dissolved in THF, and was re-precipitated in methanol of a 50-times amount of that
10 of THF required for dissolving. The precipitate was recovered and dried under a reduced pressure to obtain 5.30 g of polymer. An NMR analysis conducted under conditions same as in Example 6 for specifying the structure of the obtained polymer confirmed a
15 polyhydroxyalkanoate containing units represented by chemical formula (69) as monomer units.

[0305]

[Chemical Formula 106]



20 [0306]

An average molecular weight of the obtained polyhydroxyalkanoate was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-

GEL Super HM-H, solvent: chloroform, converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 13,200$ and a weight-averaged molecular weight $M_w = 18,300$.

5 Furthermore, in order to calculate the units of the obtained polyhydroxyalkanoate, the calculation was made by methyl esterification of the carboxyl group at the end of the side chain of the polyhydroxyalkanoate using trimethylsilyl diazomethane. 30 mg of the targeted
10 polyhydroxyalkanoate were placed in a 100-ml eggplant-shaped flask and dissolved by adding 2.1 ml of chloroform and 0.7 ml of methanol. Then 0.5 ml of a 2 mol/L hexane solution of trimethylsilyl diazomethane were added and the mixture was agitated for 1 hour at
15 the room temperature. After the reaction, the solvent was distilled off to recover the polymer. The polymer was washed with 50 ml of methanol, then recovered, and dried under a reduced pressure to obtain 28 mg of polyhydroxyalkanoate.

20 [0307]

An NMR analysis conducted under conditions same as in Example 6 confirmed that a proportion of the units of the polyhydroxyalkanoate represented by chemical formula (69) was a copolymer as unit C by 8 mol% and
25 unit D by 92 mol%.

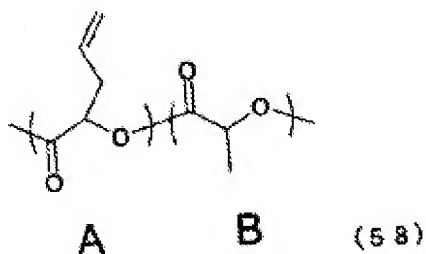
[0308]

(Example 25)

Oxidation reaction of a polyhydroxyalkanoate constituted of a unit represented by chemical formula (58) synthesized in Example 13

[0309]

5 [Chemical Formula 107]



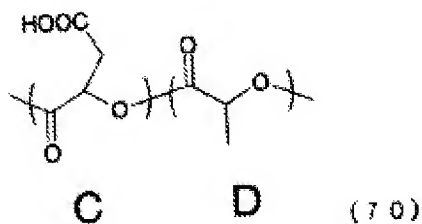
[0310]

0.50 g of polyhydroxyalkanoate copolymer (A: 4 mol%, B: 96 mol%) obtained in Example 13 and
10 constituted of a unit represented by chemical formula (58) were placed in an eggplant-shaped flask, and dissolved by adding 30 ml of acetone. The solution was placed in an ice bath and agitated while added 5 ml of acetic acid and 0.22 g of 18-crown-6-ether. Then 0.17
15 g of potassium permanganate was slowly added in the ice bath and the mixture was agitated for 2 hours in the ice bath and further 18 hours at the room temperature. After the reaction, 60 ml of ethyl acetate and further 45 ml of water were added. Next, sodium hydrogen
20 sulfite was added until overacidity was removed. Then, the liquid factor was made to pH = 1 by 1.0 N of hydrochloric acid. The organic layer was separated.

The organic layer was recovered and washed three times with 1.0 N of hydrochloric acid. After recovering the organic layer, the solvent was distilled off to recover a crude polymer. Next, the polymer was recovered after
5 cleaning with 50 ml of water and 50 ml of methanol, and then cleaning three times with 50 ml of water. It was then dissolved in THF, and was re-precipitated in methanol of a 50-times amount of that of THF required for dissolving. The precipitate was recovered and
10 dried under a reduced pressure to obtain 0.45 g of polymer. An NMR analysis conducted under conditions same as in Example 6 for specifying the structure of the obtained polymer confirmed a polyhydroxyalkanoate containing units represented by chemical formula (70)
15 as monomer units.

[0311]

[Chemical Formula 108]



[0312]

20 An average molecular weight of the obtained polyhydroxyalkanoate was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-

GEL Super HM-H, solvent: chloroform, converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 12,800$ and a weight-averaged molecular weight $M_w = 16,500$.

5 Furthermore, in order to calculate the units of the obtained polyhydroxyalkanoate, the calculation was made by methyl esterification of the carboxyl group at the end of the side chain of the polyhydroxyalkanoate using trimethylsilyl diazomethane. 30 mg of the targeted
10 polyhydroxyalkanoate were placed in a 100-ml eggplant-shaped flask and dissolved by adding 2.1 ml of chloroform and 0.7 ml of methanol. Then 0.5 ml of a 2 mol/L hexane solution of trimethylsilyl diazomethane were added and the mixture was agitated for 1 hour at
15 the room temperature. After the reaction, the solvent was distilled off to recover the polymer. The polymer was washed with 50 ml of methanol, then recovered, and dried under a reduced pressure to obtain 29 mg of polyhydroxyalkanoate.

20 [0313]

An NMR analysis conducted under conditions same as in Example 6 confirmed that a proportion of the units of the polyhydroxyalkanoate represented by chemical formula (70) was a copolymer as unit C by 4 mol% and
25 unit D by 96 mol%.

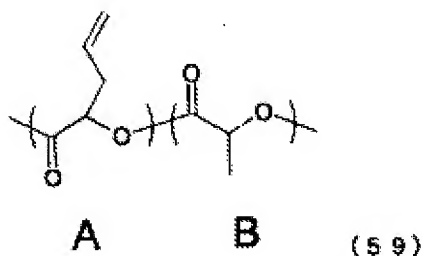
[0314]

(Example 26)

Oxidation reaction of a polyhydroxyalkanoate constituted of a unit represented by chemical formula (59) synthesized in Example 14

[0315]

5 [Chemical Formula 109]



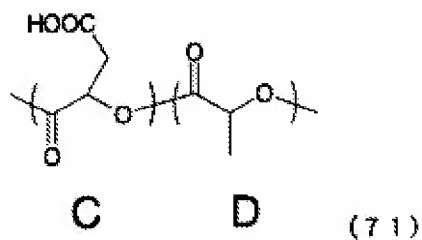
[0316]

0.50 g of polyhydroxyalkanoate copolymer (A: 14 mol%, B: 86 mol%) obtained in Example 14 and constituted of a unit represented by chemical formula (59) were placed in an eggplant-shaped flask, and dissolved by adding 30 ml of acetone. The solution was placed in an ice bath and agitated while added 5 ml of acetic acid and 0.73 g of 18-crown-6-ether. Then 0.58 g of potassium permanganate was slowly added in the ice bath and the mixture was agitated for 2 hours in the ice bath and further 18 hours at the room temperature. After the reaction, 60 ml of ethyl acetate and further 45 ml of water were added. Next, sodium hydrogen sulfite was added until overacidity was removed. Then, the liquid factor was made to pH = 1 by 1.0 N of hydrochloric acid. The organic layer was separated.

The organic layer was recovered and washed three times with 1.0 N of hydrochloric acid. After recovering the organic layer, the solvent was distilled off to recover a crude polymer. Next, the polymer was recovered after
5 cleaning with 50 ml of water and 50 ml of methanol, and then cleaning three times with 50 ml of water. It was then dissolved in THF, and was re-precipitated in methanol of a 50-times amount of that of THF required for dissolving. The precipitate was recovered and
10 dried under a reduced pressure to obtain 0.44 g of polymer. An NMR analysis conducted under conditions same as in Example 6 for specifying the structure of the obtained polymer confirmed a polyhydroxyalkanoate containing units represented by chemical formula (71)
15 as monomer units.

[0317]

[Chemical Formula 110]



[0318]

20 An average molecular weight of the obtained polyhydroxyalkanoate was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-

GEL Super HM-H, solvent: chloroform, converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 10,600$ and a weight-averaged molecular weight $M_w = 13,800$.

5 Furthermore, in order to calculate the units of the obtained polyhydroxyalkanoate, the calculation was made by methyl esterification of the carboxyl group at the end of the side chain of the polyhydroxyalkanoate using trimethylsilyl diazomethane. 30 mg of the targeted
10 polyhydroxyalkanoate were placed in a 100-ml eggplant-shaped flask and dissolved by adding 2.1 ml of chloroform and 0.7 ml of methanol. Then 0.5 ml of a 2 mol/L hexane solution of trimethylsilyl diazomethane were added and the mixture was agitated for 1 hour at
15 the room temperature. After the reaction, the solvent was distilled off to recover the polymer. The polymer was washed with 50 ml of methanol, then recovered, and dried under a reduced pressure to obtain 27 mg of polyhydroxyalkanoate.

20 [0319]

An NMR analysis conducted under conditions same as in Example 6 confirmed that a proportion of the units of the polyhydroxyalkanoate represented by chemical formula (71) was a copolymer as unit C by 138 mol% and
25 unit D by 87 mol%.

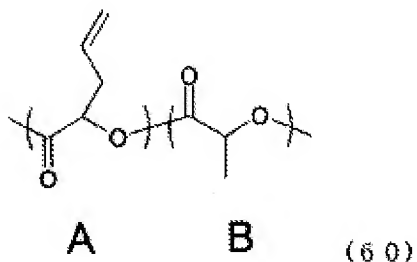
[0320]

(Example 27)

Oxidation reaction of a polyhydroxyalkanoate constituted of a unit represented by chemical formula (60) synthesized in Example 15

[0321]

5 [Chemical Formula 111]



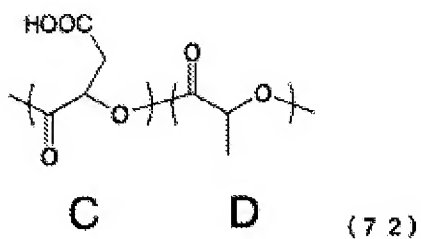
[0322]

0.50 g of polyhydroxyalkanoate copolymer (A: 18 mol%, B: 82 mol%) obtained in Example 15 and constituted of a unit represented by chemical formula (60) were placed in an eggplant-shaped flask, and dissolved by adding 30 ml of acetone. The solution was placed in an ice bath and agitated while added 5 ml of acetic acid and 0.93 g of 18-crown-6-ether. Then 0.74 g of potassium permanganate was slowly added in the ice bath and the mixture was agitated for 2 hours in the ice bath and further 18 hours at the room temperature. After the reaction, 60 ml of ethyl acetate and further 45 ml of water were added. Next, sodium hydrogen sulfite was added until overacidity was removed. Then, the liquid factor was made to pH = 1 by 1.0 N of hydrochloric acid. The organic layer was separated.

The organic layer was recovered and washed three times with 1.0 N of hydrochloric acid. After recovering the organic layer, the solvent was distilled off to recover a crude polymer. Next, the polymer was recovered after
5 cleaning with 50 ml of water and 50 ml of methanol, and then cleaning three times with 50 ml of water. It was then dissolved in THF, and was re-precipitated in methanol of a 50-times amount of that of THF required for dissolving. The precipitate was recovered and
10 dried under a reduced pressure to obtain 0.43 g of polymer. An NMR analysis conducted under conditions same as in Example 6 for specifying the structure of the obtained polymer confirmed a polyhydroxyalkanoate containing units represented by chemical formula (72)
15 as monomer units.

[0323]

[Chemical Formula 112]



[0324]

20 An average molecular weight of the obtained polyhydroxyalkanoate was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-

GEL Super HM-H, solvent: chloroform, converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 10,100$ and a weight-averaged molecular weight $M_w = 13,200$.

5 Furthermore, in order to calculate the units of the obtained polyhydroxyalkanoate, the calculation was made by methyl esterification of the carboxyl group at the end of the side chain of the polyhydroxyalkanoate using trimethylsilyl diazomethane. 30 mg of the targeted
10 polyhydroxyalkanoate were placed in a 100-ml eggplant-shaped flask and dissolved by adding 2.1 ml of chloroform and 0.7 ml of methanol. Then 0.5 ml of a 2 mol/L hexane solution of trimethylsilyl diazomethane were added and the mixture was agitated for 1 hour at
15 the room temperature. After the reaction, the solvent was distilled off to recover the polymer. The polymer was washed with 50 ml of methanol, then recovered, and dried under a reduced pressure to obtain 28 mg of polyhydroxyalkanoate.

20 [0325]

An NMR analysis conducted under conditions same as in Example 6 confirmed that a proportion of the units of the polyhydroxyalkanoate represented by chemical formula (72) was a copolymer as unit C by 16 mol% and
25 unit D by 84 mol%.

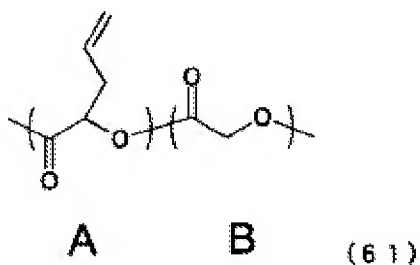
[0326]

(Example 28)

Oxidation reaction of a polyhydroxyalkanoate constituted of a unit represented by chemical formula (61) synthesized in Example 16

[0327]

5 [Chemical Formula 113]



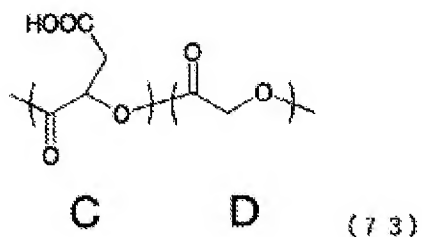
[0328]

0.50 g of polyhydroxyalkanoate copolymer (A: 10 mol%, B: 90 mol%) obtained in Example 16 and constituted of a unit represented by chemical formula (61) were placed in an eggplant-shaped flask, and dissolved by adding 30 ml of acetone. The solution was placed in an ice bath and agitated while added 5 ml of acetic acid and 0.64 g of 18-crown-6-ether. Then 0.51 g of potassium permanganate was slowly added in the ice bath and the mixture was agitated for 2 hours in the ice bath and further 18 hours at the room temperature. After the reaction, 60 ml of ethyl acetate and further 45 ml of water were added. Next, sodium hydrogen sulfite was added until overacidity was removed. Then, the liquid factor was made to pH = 1 by 1.0 N of hydrochloric acid. The organic layer was separated.

The organic layer was recovered and washed three times with 1.0 N of hydrochloric acid. After recovering the organic layer, the solvent was distilled off to recover a crude polymer. Next, the polymer was recovered after
5 cleaning with 50 ml of water and 50 ml of methanol, and then cleaning three times with 50 ml of water. It was then dissolved in THF, and was re-precipitated in methanol of a 50-times amount of that of THF required for dissolving. The precipitate was recovered and
10 dried under a reduced pressure to obtain 0.44 g of polymer. An NMR analysis conducted under conditions same as in Example 6 for specifying the structure of the obtained polymer confirmed a polyhydroxyalkanoate containing units represented by chemical formula (73)
15 as monomer units.

[0329]

[Chemical Formula 114]



[0330]

20 An average molecular weight of the obtained polyhydroxyalkanoate was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-

GEL Super HM-H, solvent: chloroform, converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 13,200$ and a weight-averaged molecular weight $M_w = 17,700$.

5 Furthermore, in order to calculate the units of the obtained polyhydroxyalkanoate, the calculation was made by methyl esterification of the carboxyl group at the end of the side chain of the polyhydroxyalkanoate using trimethylsilyl diazomethane. 30 mg of the targeted
10 polyhydroxyalkanoate were placed in a 100-ml eggplant-shaped flask and dissolved by adding 2.1 ml of chloroform and 0.7 ml of methanol. Then 0.5 ml of a 2 mol/L hexane solution of trimethylsilyl diazomethane were added and the mixture was agitated for 1 hour at
15 the room temperature. After the reaction, the solvent was distilled off to recover the polymer. The polymer was washed with 50 ml of methanol, then recovered, and dried under a reduced pressure to obtain 30 mg of polyhydroxyalkanoate.

20 [0331]

An NMR analysis conducted under conditions same as in Example 6 confirmed that a proportion of the units of the polyhydroxyalkanoate represented by chemical formula (73) was a copolymer as unit C by 9 mol% and
25 unit D by 91 mol%.

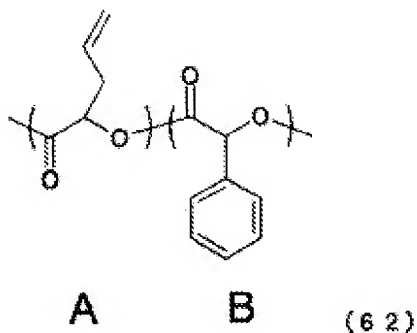
[0332]

(Example 29)

Oxidation reaction of a polyhydroxyalkanoate constituted of a unit represented by chemical formula (62) synthesized in Example 17

[0333]

5 [Chemical Formula 115]



[0334]

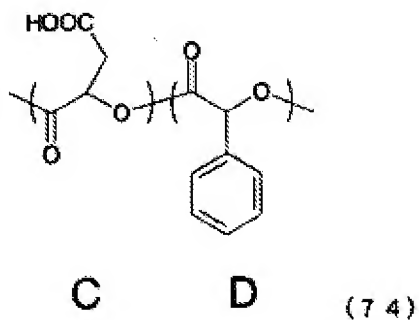
0.50 g of polyhydroxyalkanoate copolymer (A: 8 mol%, B: 92 mol%) obtained in Example 17 and constituted of a unit represented by chemical formula (62) were placed in an eggplant-shaped flask, and dissolved by adding 30 ml of acetone. The solution was placed in an ice bath and agitated while added 5 ml of acetic acid and 0.24 g of 18-crown-6-ether. Then 0.19 g of potassium permanganate was slowly added in the ice bath and the mixture was agitated for 2 hours in the ice bath and further 18 hours at the room temperature. After the reaction, 60 ml of ethyl acetate and further 45 ml of water were added. Next, sodium hydrogen sulfite was added until overacidity was removed. Then, the liquid factor was made to pH = 1 by 1.0 N of

10
15
20

hydrochloric acid. The organic layer was separated.
The organic layer was recovered and washed three times
with 1.0 N of hydrochloric acid. After recovering the
organic layer, the solvent was distilled off to recover
5 a crude polymer. Next, the polymer was recovered after
cleaning with 50 ml of water and 50 ml of methanol, and
then cleaning three times with 50 ml of water. It was
then dissolved in THF, and was re-precipitated in
methanol of a 50-times amount of that of THF required
10 for dissolving. The precipitate was recovered and
dried under a reduced pressure to obtain 0.44 g of
polymer. An NMR analysis conducted under conditions
same as in Example 6 for specifying the structure of
the obtained polymer confirmed a polyhydroxyalkanoate
15 containing units represented by chemical formula (74)
as monomer units.

[0335]

[Chemical Formula 116]



20 [0336]

An average molecular weight of the obtained

polyhydroxyalkanoate was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-GEL Super HM-H, solvent: chloroform, converted as polystyrene). As a result, there were obtained a
5 number-averaged molecular weight $M_n = 12,500$ and a weight-averaged molecular weight $M_w = 24,300$.

[0337]

Furthermore, in order to calculate the units of the obtained polyhydroxyalkanoate, the calculation was
10 made by methyl esterification of the carboxyl group at the end of the side chain of the polyhydroxyalkanoate using trimethylsilyl diazomethane. 30 mg of the targeted polyhydroxyalkanoate were placed in a 100-ml eggplant-shaped flask and dissolved by adding 2.1 ml of
15 chloroform and 0.7 ml of methanol. Then 0.5 ml of a 2 mol/L hexane solution of trimethylsilyl diazomethane were added and the mixture was agitated for 1 hour at the room temperature. After the reaction, the solvent was distilled off to recover the polymer. The polymer
20 was washed with 50 ml of methanol, then recovered, and dried under a reduced pressure to obtain 29 mg of polyhydroxyalkanoate.

[0338]

An NMR analysis conducted under conditions same as
25 in Example 6 confirmed that a proportion of the units of the polyhydroxyalkanoate represented by chemical formula (74) was a copolymer as unit C by 7 mol% and

unit D by 93 mol%.

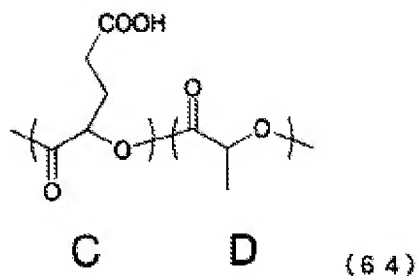
[0339]

(Example 30)

Condensation reaction of a polyhydroxyalkanoate
5 constituted of a unit represented by chemical formula
(64) synthesized in Example 19 with 2-
aminobenzenesulfonic acid

[0340]

[Chemical Formula 117]



10

[0341]

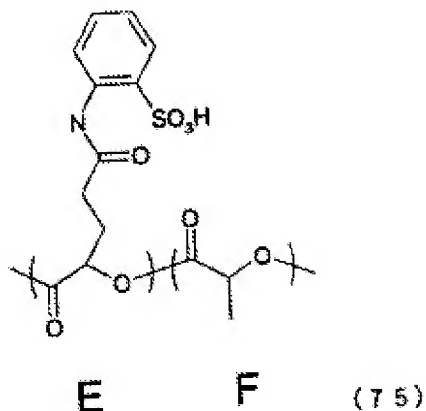
In a nitrogen atmosphere, 0.40 g of polymer
synthesized with polyhydroxyalkanoate copolymer (C: 8
mol%, D: 92 mol%) obtained in Example 19 and
15 constituted of a unit represented by chemical formula
(64) and 0.36 g of 2-aminobenzenesulfonic acid were
placed in a 100-ml three-necked flask, agitated with
15.0 ml of pyridine, further added with 1.09 ml of
triphenyl phosphite and heated for 6 hours at 120°C.
20 After the reaction, the polymer was recovered by a re-
precipitation in 150 ml of ethanol. The obtained

polymer was washed with 1N hydrochloric acid for 1 day,
then washed by an agitation in water for 1 day and
dried under a reduced pressure to obtain 0.32 g of a
polymer. The structure of the obtained polymer was
5 analyzed by ^1H -NMR (FT-NMR: Bruker DPX 400, resonance
frequency: 400 MHz, measured species: ^1H , solvent:
deuterized DMSO, temperature: room temperature) and a
Fourier transformed infrared absorption (FT-IR)
spectrum (Nicolet AVATAR 360FT-IR). The IR measurement
10 showed a decrease of a peak at 1695 cm^{-1} attributable
to a carboxylic acid, and a new peak at 1658 cm^{-1}
attributable to an amide group.

A result of ^1H -NMR confirmed, by a shift in a peak
resulting from an aromatic ring of the 2-
15 aminobenzenesulfonic acid structure, that the polymer
was a polyhydroxyalkanoate containing units represented
by chemical formula (75) as monomer units.

[0342]

[Chemical Formula 118]



[0343]

It was also confirmed that a proportion of the units of the polyhydroxyalkanoate represented by chemical formula (75) was a copolymer as unit E by 8 mol% and unit F by 92 mol%. An average molecular weight of the obtained polymer was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8120, column: Polymer Laboratories PLgel 5 μ MIXED-C, solvent: DMF/LiBr 0.1 % (w/v), converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 11,300$ and a weight-averaged molecular weight $M_w = 16,000$.

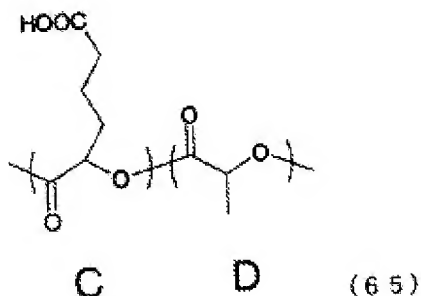
[0344]

15 (Example 31)

Condensation reaction of a polyhydroxyalkanoate constituted of a unit represented by chemical formula (65) synthesized in Example 20 with 2-aminobenzenesulfonic acid

[0345]

[Chemical Formula 119]



[0346]

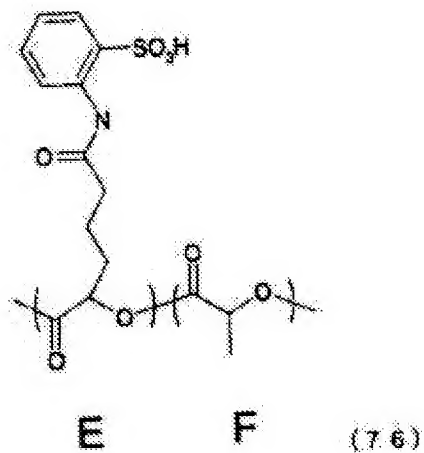
5 In a nitrogen atmosphere, 0.40 g of polymer
synthesized with polyhydroxyalkanoate copolymer (C: 8
mol%, D: 92 mol%) obtained in Example 20 and
constituted of a unit represented by chemical formula
(65) and 0.36 g of 2-aminobenzenesulfonic acid were
10 placed in a 100-ml three-necked flask, agitated with
15.0 ml of pyridine, further added with 1.07 ml of
triphenyl phosphite and heated for 6 hours at 120°C.
After the reaction, the polymer was recovered by a re-
precipitation in 150 ml of ethanol. The obtained
15 polymer was washed with 1N hydrochloric acid for 1 day,
then washed by an agitation in water for 1 day and
dried under a reduced pressure to obtain 0.33 g of a
polymer. The structure of the obtained polymer was
analyzed by ¹H-NMR (FT-NMR: Bruker DPX 400, resonance
20 frequency: 400 MHz, measured species: ¹H, solvent:
deuterized DMSO, temperature: room temperature) and a
Fourier transformed infrared absorption (FT-IR)

spectrum (Nicolet AVATAR 360FT-IR). The IR measurement showed a decrease of a peak at 1695 cm^{-1} attributable to a carboxylic acid, and a new peak at 1658 cm^{-1} attributable to an amide group.

5 A result of ^1H -NMR confirmed, by a shift in a peak resulting from an aromatic ring of the 2-aminobenzenesulfonic acid structure, that the polymer was a polyhydroxyalkanoate containing units represented by chemical formula (76) as monomer units.

10 [0347]

[Chemical Formula 120]



[0348]

15 It was also confirmed that a proportion of the units of the polyhydroxyalkanoate represented by chemical formula (76) was a copolymer as unit E by 8 mol% and unit F by 92 mol%. An average molecular weight of the obtained polymer was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8120, column:

Polymer Laboratories PLgel 5 μ MIXED-C, solvent:
DMF/LiBr 0.1 %(w/v), converted as polystyrene). As a
result, there were obtained a number-averaged molecular
weight $M_n = 11,500$ and a weight-averaged molecular
5 weight $M_w = 17,300$.

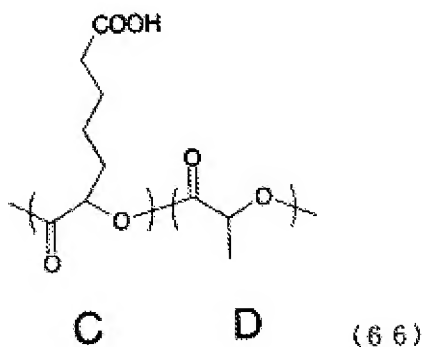
[0349]

(Example 32)

Condensation reaction of a polyhydroxyalkanoate
constituted of a unit represented by chemical formula
10 (66) synthesized in Example 21 with 2-
aminobenzenesulfonic acid

[0350]

[Chemical Formula 121]



15 [0351]

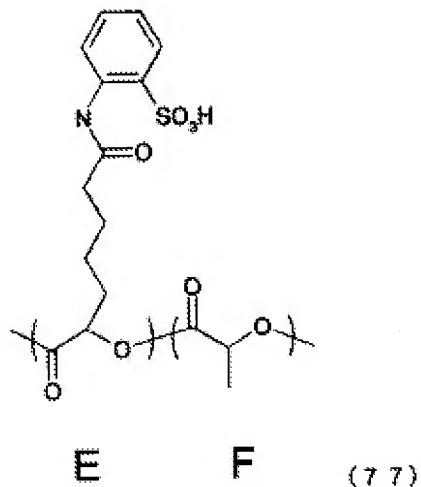
In a nitrogen atmosphere, 0.40 g of polymer
synthesized with polyhydroxyalkanoate copolymer (C: 8
mol%, D: 92 mol%) obtained in Example 21 and
constituted of a unit represented by chemical formula
20 (66) and 0.35 g of 2-aminobenzenesulfonic acid were
placed in a 100-ml three-necked flask, agitated with

15.0 ml of pyridine, further added with 1.06 ml of triphenyl phosphite and heated for 6 hours at 120°C. After the reaction, the polymer was recovered by a re-precipitation in 150 ml of ethanol. The obtained
5 polymer was washed with 1N hydrochloric acid for 1 day, then washed by an agitation in water for 1 day and dried under a reduced pressure to obtain 0.34 g of a polymer. The structure of the obtained polymer was analyzed by ^1H -NMR (FT-NMR: Bruker DPX 400, resonance
10 frequency: 400 MHz, measured species: ^1H , solvent: deuterized DMSO, temperature: room temperature) and a Fourier transformed infrared absorption (FT-IR) spectrum (Nicolet AVATAR 360FT-IR). The IR measurement showed a decrease of a peak at 1695 cm^{-1} attributable
15 to a carboxylic acid, and a new peak at 1658 cm^{-1} attributable to an amide group.

A result of ^1H -NMR confirmed, by a shift in a peak resulting from an aromatic ring of the 2-aminobenzenesulfonic acid structure, that the polymer
20 was a polyhydroxyalkanoate containing units represented by chemical formula (77) as monomer units.

[0352]

[Chemical Formula 122]



[0353]

It was also confirmed that a proportion of the units of the polyhydroxyalkanoate represented by chemical formula (77) was a copolymer as unit E by 8 mol% and unit F by 92 mol%. An average molecular weight of the obtained polymer was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8120, column: Polymer Laboratories PLgel 5 μ MIXED-C, solvent: DMF/LiBr 0.1 % (w/v), converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 10,100$ and a weight-averaged molecular weight $M_w = 14,300$.

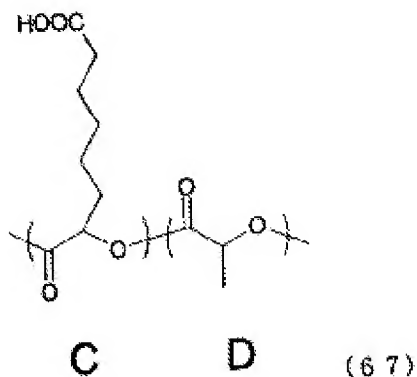
[0354]

(Example 33)

Condensation reaction of a polyhydroxyalkanoate constituted of a unit represented by chemical formula (67) synthesized in Example 22 with 2-aminobenzenesulfonic acid

[0355]

[Chemical Formula 123]



[0356]

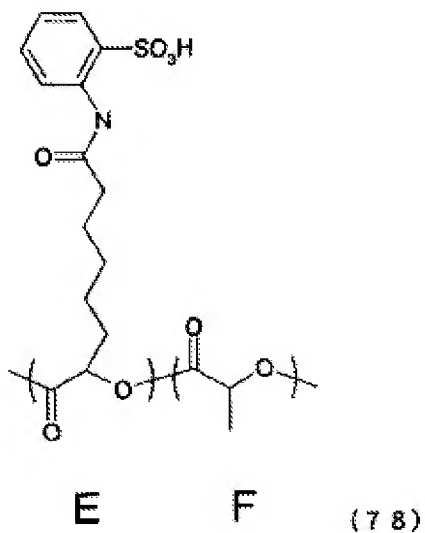
5 In a nitrogen atmosphere, 0.40 g of polymer synthesized with polyhydroxyalkanoate copolymer (C: 7 mol%, D: 93 mol%) obtained in Example 22 and constituted of a unit represented by chemical formula (67) and 0.31 g of 2-aminobenzenesulfonic acid were
10 placed in a 100-ml three-necked flask, agitated with 15.0 ml of pyridine, further added with 0.92 ml of triphenyl phosphite and heated for 6 hours at 120°C. After the reaction, the polymer was recovered by a re-precipitation in 150 ml of ethanol. The obtained
15 polymer was washed with 1N hydrochloric acid for 1 day, then washed by an agitation in water for 1 day and dried under a reduced pressure to obtain 0.33 g of a polymer. The structure of the obtained polymer was analyzed by ¹H-NMR (FT-NMR: Bruker DPX 400, resonance
20 frequency: 400 MHz, measured species: ¹H, solvent: deuterized DMSO, temperature: room temperature) and a

Fourier transformed infrared absorption (FT-IR) spectrum (Nicolet AVATAR 360FT-IR). The IR measurement showed a decrease of a peak at 1695 cm^{-1} attributable to a carboxylic acid, and a new peak at 1658 cm^{-1} attributable to an amide group.

A result of ^1H -NMR confirmed, by a shift in a peak resulting from an aromatic ring of the 2-aminobenzenesulfonic acid structure, that the polymer was a polyhydroxyalkanoate containing units represented by chemical formula (78) as monomer units.

[0357]

[Chemical Formula 124]



[0358]

It was also confirmed that a proportion of the units of the polyhydroxyalkanoate represented by chemical formula (78) was a copolymer as unit E by 7 mol% and unit F by 93 mol%. An average molecular

weight of the obtained polymer was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8120, column: Polymer Laboratories PLgel 5 μ MIXED-C, solvent: DMF/LiBr 0.1 % (w/v), converted as polystyrene). As a
5 result, there were obtained a number-averaged molecular weight $M_n = 9,900$ and a weight-averaged molecular weight $M_w = 14,400$.

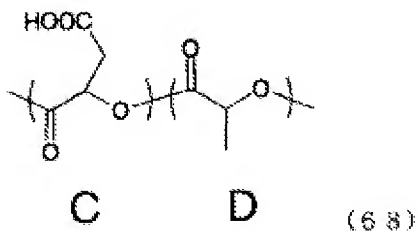
[0359]

(Example 34)

10 Condensation reaction of a polyhydroxyalkanoate constituted of a unit represented by chemical formula (68) synthesized in Example 23 with 2-aminobenzenesulfonic acid

[0360]

15 [Chemical Formula 125]



[0361]

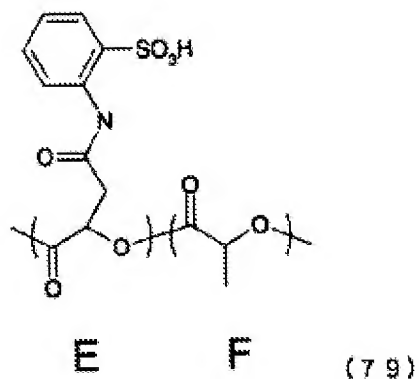
In a nitrogen atmosphere, 0.40 g of polymer synthesized with polyhydroxyalkanoate copolymer (C: 8
20 mol%, D: 92 mol%) obtained in Example 23 and constituted of a unit represented by chemical formula (68) and 0.37 g of 2-aminobenzenesulfonic acid were

placed in a 100-ml three-necked flask, agitated with
15.0 ml of pyridine, further added with 1.10 ml of
triphenyl phosphite and heated for 6 hours at 120°C.
After the reaction, the polymer was recovered by a re-
5 precipitation in 150 ml of ethanol. The obtained
polymer was washed with 1N hydrochloric acid for 1 day,
then washed by an agitation in water for 1 day and
dried under a reduced pressure to obtain 0.32 g of a
polymer. The structure of the obtained polymer was
10 analyzed by ^1H -NMR (FT-NMR: Bruker DPX 400, resonance
frequency: 400 MHz, measured species: ^1H , solvent:
deuterized DMSO, temperature: room temperature) and a
Fourier transformed infrared absorption (FT-IR)
spectrum (Nicolet AVATAR 360FT-IR). The IR measurement
15 showed a decrease of a peak at 1695 cm^{-1} attributable
to a carboxylic acid, and a new peak at 1658 cm^{-1}
attributable to an amide group.

A result of ^1H -NMR confirmed, by a shift in a peak
resulting from an aromatic ring of the 2-
20 aminobenzenesulfonic acid structure, that the polymer
was a polyhydroxyalkanoate containing units represented
by chemical formula (79) as monomer units.

[0362]

[Chemical Formula 126]



[0363]

It was also confirmed that a proportion of the units of the polyhydroxyalkanoate represented by chemical formula (79) was a copolymer as unit E by 8 mol% and unit F by 92 mol%. An average molecular weight of the obtained polymer was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8120, column: Polymer Laboratories PLgel 5 μ MIXED-C, solvent: DMF/LiBr 0.1 % (w/v), converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 11,800$ and a weight-averaged molecular weight $M_w = 16,600$.

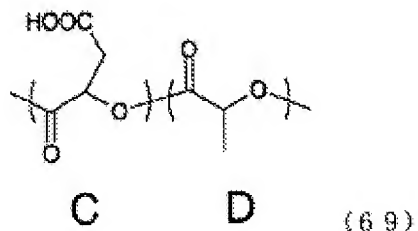
[0364]

(Example 35)

Condensation reaction of a polyhydroxyalkanoate constituted of a unit represented by chemical formula (69) synthesized in Example 24 with p-toluidine-2-sulfonic acid

[0365]

[Chemical Formula 127]



[0366]

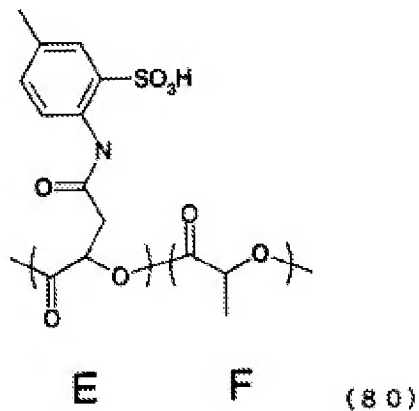
In a nitrogen atmosphere, 0.40 g of polymer
5 synthesized with polyhydroxyalkanoate copolymer (C: 8
mol%, D: 92 mol%) obtained in Example 24 and
constituted of a unit represented by chemical formula
(69) and 0.39 g of p-toluidine-2-sulfonic acid were
placed in a 100-ml three-necked flask, agitated with
10 15.0 ml of pyridine, further added with 1.10 ml of
triphenyl phosphite and heated for 6 hours at 120°C.
After the reaction, the polymer was recovered by a re-
precipitation in 150 ml of ethanol. The obtained
polymer was washed with 1N hydrochloric acid for 1 day,
15 then washed by an agitation in water for 1 day and
dried under a reduced pressure to obtain 0.33 g of a
polymer. The structure of the obtained polymer was
analyzed by ¹H-NMR (FT-NMR: Bruker DPX 400, resonance
frequency: 400 MHz, measured species: ¹H, solvent:
20 deuterized DMSO, temperature: room temperature) and a
Fourier transformed infrared absorption (FT-IR)
spectrum (Nicolet AVATAR 360FT-IR). The IR measurement
showed a decrease of a peak at 1695 cm⁻¹ attributable

to a carboxylic acid, and a new peak at 1658 cm^{-1} attributable to an amide group.

A result of $^1\text{H-NMR}$ confirmed, by a shift in a peak resulting from an aromatic ring of the p-toluidine-2-sulfonic acid structure, that the polymer was a polyhydroxyalkanoate containing units represented by chemical formula (80) as monomer units.

[0367]

[Chemical Formula 128]



10

[0368]

It was also confirmed that a proportion of the units of the polyhydroxyalkanoate represented by chemical formula (80) was a copolymer as unit E by 8 mol% and unit F by 92 mol%. An average molecular weight of the obtained polymer was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8120, column: Polymer Laboratories PLgel 5μ MIXED-C, solvent: DMF/LiBr 0.1 % (w/v), converted as polystyrene). As a

result, there were obtained a number-averaged molecular weight $M_n = 11,000$ and a weight-averaged molecular weight $M_w = 15,700$.

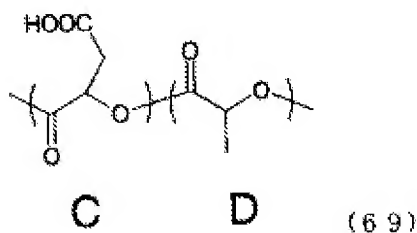
[0369]

5 (Example 36)

Condensation reaction of a polyhydroxyalkanoate constituted of a unit represented by chemical formula (69) synthesized in Example 24 with 4-aminobenzenesulfonic acid

10 [0370]

[Chemical Formula 129]



[0371]

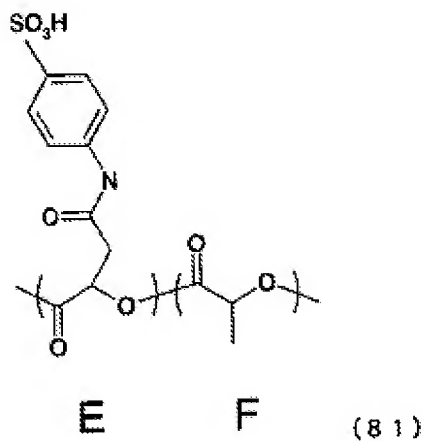
In a nitrogen atmosphere, 0.40 g of polymer
15 synthesized with polyhydroxyalkanoate copolymer (C: 8 mol%, D: 92 mol%) obtained in Example 24 and constituted of a unit represented by chemical formula (69) and 0.37 g of 4-aminobenzenesulfonic acid were placed in a 100-ml three-necked flask, agitated with
20 15.0 ml of pyridine, further added with 1.10 ml of triphenyl phosphite and heated for 6 hours at 120°C. After the reaction, the polymer was recovered by a re-precipitation in 150 ml of ethanol. The obtained

polymer was washed with 1N hydrochloric acid for 1 day,
then washed by an agitation in water for 1 day and
dried under a reduced pressure to obtain 0.31 g of a
polymer. The structure of the obtained polymer was
5 analyzed by ^1H -NMR (FT-NMR: Bruker DPX 400, resonance
frequency: 400 MHz, measured species: ^1H , solvent:
deuterized DMSO, temperature: room temperature) and a
Fourier transformed infrared absorption (FT-IR)
spectrum (Nicolet AVATAR 360FT-IR). The IR measurement
10 showed a decrease of a peak at 1695 cm^{-1} attributable
to a carboxylic acid, and a new peak at 1658 cm^{-1}
attributable to an amide group.

A result of ^1H -NMR confirmed, by a shift in a peak
resulting from an aromatic ring of the 4-
15 aminobenzenesulfonic acid structure, that the polymer
was a polyhydroxyalkanoate containing units represented
by chemical formula (81) as monomer units.

[0372]

[Chemical Formula 130]



[0373]

It was also confirmed that a proportion of the units of the polyhydroxyalkanoate represented by chemical formula (81) was a copolymer as unit E by 8
5 mol% and unit F by 92 mol%. An average molecular weight of the obtained polymer was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8120, column: Polymer Laboratories PLgel 5 μ MIXED-C, solvent: DMF/LiBr 0.1 % (w/v), converted as polystyrene). As a
10 result, there were obtained a number-averaged molecular weight $M_n = 10,700$ and a weight-averaged molecular weight $M_w = 15,700$.

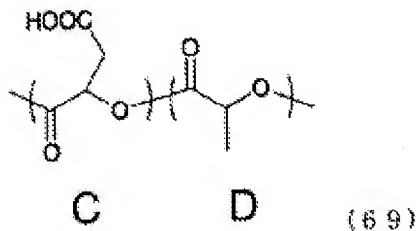
[0374]

(Example 37)

15 Condensation reaction of a polyhydroxyalkanoate constituted of a unit represented by chemical formula (69) synthesized in Example 24 with 3-aminobenzenesulfonic acid

[0375]

20 [Chemical Formula 131]



[0376]

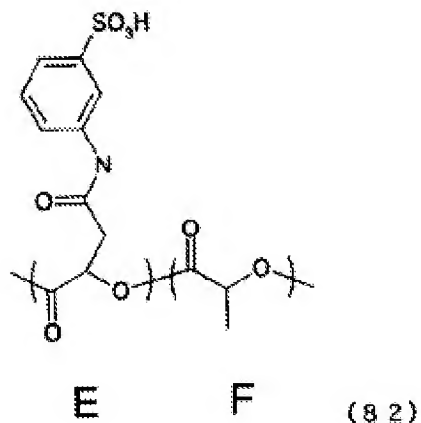
In a nitrogen atmosphere, 0.40 g of polymer

synthesized with polyhydroxyalkanoate copolymer (C: 8 mol%, D: 92 mol%) obtained in Example 24 and constituted of a unit represented by chemical formula (69) and 0.37 g of 3-aminobenzenesulfonic acid were placed in a 100-ml three-necked flask, agitated with 15.0 ml of pyridine, further added with 1.10 ml of triphenyl phosphite and heated for 6 hours at 120°C. After the reaction, the polymer was recovered by a re-precipitation in 150 ml of ethanol. The obtained polymer was washed with 1N hydrochloric acid for 1 day, then washed by an agitation in water for 1 day and dried under a reduced pressure to obtain 0.32 g of a polymer. The structure of the obtained polymer was analyzed by ^1H -NMR (FT-NMR: Bruker DPX 400, resonance frequency: 400 MHz, measured species: ^1H , solvent: deuterized DMSO, temperature: room temperature) and a Fourier transformed infrared absorption (FT-IR) spectrum (Nicolet AVATAR 360FT-IR). The IR measurement showed a decrease of a peak at 1695 cm^{-1} attributable to a carboxylic acid, and a new peak at 1658 cm^{-1} attributable to an amide group.

A result of ^1H -NMR confirmed, by a shift in a peak resulting from an aromatic ring of the 3-aminobenzenesulfonic acid structure, that the polymer was a polyhydroxyalkanoate containing units represented by chemical formula (82) as monomer units.

[0377]

[Chemical Formula 132]



[0378]

It was also confirmed that a proportion of the units of the polyhydroxyalkanoate represented by chemical formula (82) was a copolymer as unit E by 8 mol% and unit F by 92 mol%. An average molecular weight of the obtained polymer was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8120, column: Polymer Laboratories PLgel 5 μ MIXED-C, solvent: DMF/LiBr 0.1 % (w/v), converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 11,300$ and a weight-averaged molecular weight $M_w = 16,200$.

[0379]

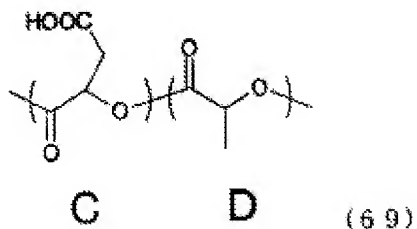
(Example 38)

Condensation reaction of a polyhydroxyalkanoate constituted of a unit represented by chemical formula (69) synthesized in Example 24 with 4-methoxyaniline-2-

sulfonic acid

[0380]

[Chemical Formula 133]



5 [0381]

In a nitrogen atmosphere, 0.40 g of polymer synthesized with polyhydroxyalkanoate copolymer (C: 8 mol%, D: 92 mol%) obtained in Example 24 and constituted of a unit represented by chemical formula (69) and 0.43 g of 4-methoxyaniline-2-sulfonic acid were placed in a 100-ml three-necked flask, agitated with 15.0 ml of pyridine, further added with 1.10 ml of triphenyl phosphite and heated for 6 hours at 120°C. After the reaction, the polymer was recovered by a re-precipitation in 150 ml of ethanol. The obtained polymer was washed with 1N hydrochloric acid for 1 day, then washed by an agitation in water for 1 day and dried under a reduced pressure to obtain 0.32 g of a polymer. The structure of the obtained polymer was analyzed by ¹H-NMR (FT-NMR: Bruker DPX 400, resonance frequency: 400 MHz, measured species: ¹H, solvent: deuterized DMSO, temperature: room temperature) and a Fourier transformed infrared absorption (FT-IR)

10

15

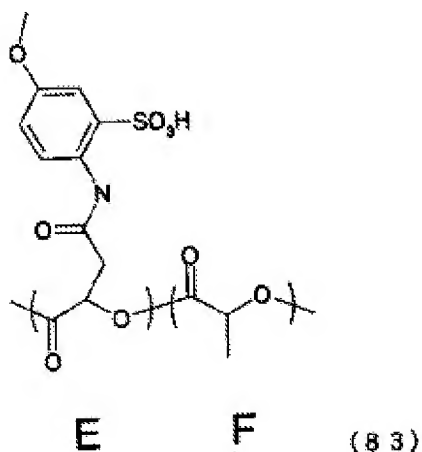
20

spectrum (Nicolet AVATAR 360FT-IR). The IR measurement showed a decrease of a peak at 1695 cm^{-1} attributable to a carboxylic acid, and a new peak at 1658 cm^{-1} attributable to an amide group.

5 A result of ^1H -NMR confirmed, by a shift in a peak resulting from an aromatic ring of the 4-methoxyaniline-2-sulfonic acid structure, that the polymer was a polyhydroxyalkanoate containing units represented by chemical formula (83) as monomer units.

10 [0382]

[Chemical Formula 134]



[0383]

15 It was also confirmed that a proportion of the units of the polyhydroxyalkanoate represented by chemical formula (83) was a copolymer as unit E by 8 mol% and unit F by 92 mol%. An average molecular weight of the obtained polymer was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8120, column:

Polymer Laboratories PLgel 5 μ MIXED-C, solvent:
DMF/LiBr 0.1 %(w/v), converted as polystyrene). As a
result, there were obtained a number-averaged molecular
weight $M_n = 11,000$ and a weight-averaged molecular
weight $M_w = 16,100$.

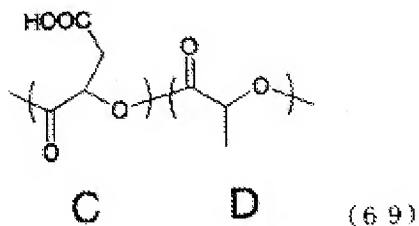
[0384]

(Example 39)

Condensation reaction of a polyhydroxyalkanoate
constituted of a unit represented by chemical formula
(69) synthesized in Example 24 with 4-
aminobenzenesulfonic acid phenyl ester

[0385]

[Chemical Formula 135]



[0386]

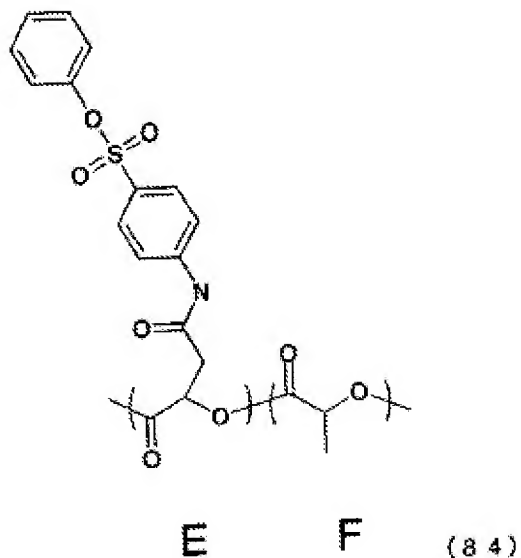
In a nitrogen atmosphere, 0.40 g of polymer
synthesized with polyhydroxyalkanoate copolymer (C: 8
mol%, D: 92 mol%) obtained in Example 24 and
constituted of a unit represented by chemical formula
(69) and 0.53 g of 4-aminobenzenesulfonic acid phenyl
ester were placed in a 100-ml three-necked flask,
agitated with 15.0 ml of pyridine, further added with
1.10 ml of triphenyl phosphite and heated for 6 hours

at 120°C. After the reaction, the polymer was recovered by a re-precipitation in 150 ml of ethanol. The obtained polymer was washed with 1N hydrochloric acid for 1 day, then washed by an agitation in water
5 for 1 day and dried under a reduced pressure to obtain 0.35 g of a polymer. The structure of the obtained polymer was analyzed by ^1H -NMR (FT-NMR: Bruker DPX 400, resonance frequency: 400 MHz, measured species: ^1H , solvent: deuterized DMSO, temperature: room
10 temperature) and a Fourier transformed infrared absorption (FT-IR) spectrum (Nicolet AVATAR 360FT-IR). The IR measurement showed a decrease of a peak at 1695 cm^{-1} attributable to a carboxylic acid, and a new peak at 1658 cm^{-1} attributable to an amide group.

15 A result of ^1H -NMR confirmed, by a shift in a peak resulting from an aromatic ring of the 4-aminobenzenesulfonic acid structure, that the polymer was a polyhydroxyalkanoate containing units represented by chemical formula (84) as monomer units.

20 [0387]

[Chemical Formula 136]



[0388]

It was also confirmed that a proportion of the units of the polyhydroxyalkanoate represented by chemical formula (84) was a copolymer as unit E by 8 mol% and unit F by 92 mol%. An average molecular weight of the obtained polymer was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8120, column: Polymer Laboratories PLgel 5 μ MIXED-C, solvent: DMF/LiBr 0.1 % (w/v), converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 11,500$ and a weight-averaged molecular weight $M_w = 17,100$.

[0389]

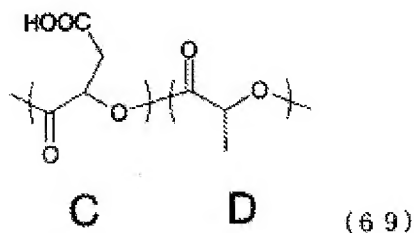
(Example 40)

Condensation reaction of a polyhydroxyalkanoate constituted of a unit represented by chemical formula

(85) synthesized in Example 24 with 2-aminobenzenesulfonic acid phenyl ester

[0390]

[Chemical Formula 137]



5

[0391]

In a nitrogen atmosphere, 0.40 g of polymer synthesized with polyhydroxyalkanoate copolymer (C: 8 mol%, D: 92 mol%) obtained in Example 24 and

10 constituted of a unit represented by chemical formula (69) and 0.53 g of 2-aminobenzenesulfonic acid phenyl ester were placed in a 100-ml three-necked flask, agitated with 15.0 ml of pyridine, further added with 1.10 ml of triphenyl phosphite and heated for 6 hours

15 at 120°C. After the reaction, the polymer was recovered by a re-precipitation in 150 ml of ethanol. The obtained polymer was washed with 1N hydrochloric acid for 1 day, then washed by an agitation in water for 1 day and dried under a reduced pressure to obtain

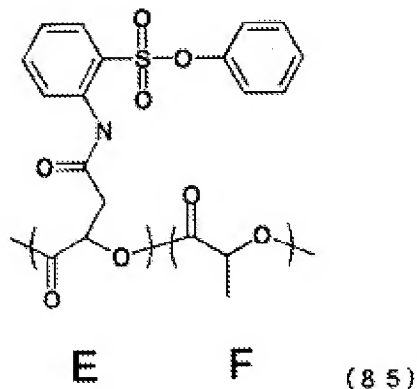
20 0.34 g of a polymer. The structure of the obtained polymer was analyzed by ¹H-NMR (FT-NMR: Bruker DPX 400, resonance frequency: 400 MHz, measured species: ¹H, solvent: deuterized DMSO, temperature: room

temperature) and a Fourier transformed infrared
absorption (FT-IR) spectrum (Nicolet AVATAR 360FT-IR).
The IR measurement showed a decrease of a peak at 1695
cm⁻¹ attributable to a carboxylic acid, and a new peak
5 at 1658 cm⁻¹ attributable to an amide group.

A result of ¹H-NMR confirmed, by a shift in a peak
resulting from an aromatic ring of the 2-
aminobenzenesulfonic acid phenyl ester structure, that
the polymer was a polyhydroxyalkanoate containing units
10 represented by chemical formula (85) as monomer units.

[0392]

[Chemical Formula 138]



[0393]

15 It was also confirmed that a proportion of the
units of the polyhydroxyalkanoate represented by
chemical formula (85) was a copolymer as unit E by 8
mol% and unit F by 92 mol%. An average molecular
weight of the obtained polymer was evaluated by gel
20 permeation chromatography (GPC: Tosoh HLC-8120, column:

Polymer Laboratories PLgel 5 μ MIXED-C, solvent:
DMF/LiBr 0.1 %(w/v), converted as polystyrene). As a
result, there were obtained a number-averaged molecular
weight $M_n = 11,300$ and a weight-averaged molecular
5 weight $M_w = 16,800$.

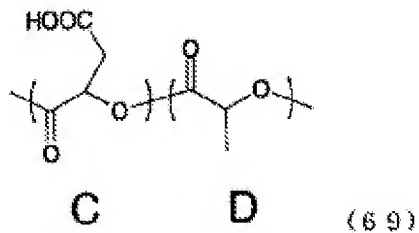
[0394]

(Example 41)

Condensation reaction of a polyhydroxyalkanoate
constituted of a unit represented by chemical formula
10 (69) synthesized in Example 24 with 2-amino-1-
naphthalenesulfonic acid

[0395]

[Chemical Formula 139]



15 [0396]

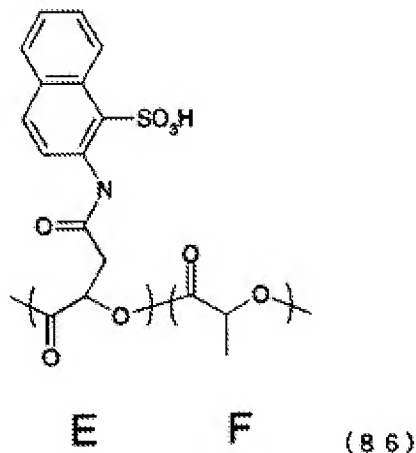
In a nitrogen atmosphere, 0.40 g of polymer
synthesized with polyhydroxyalkanoate copolymer (C: 8
mol%, D: 92 mol%) obtained in Example 24 and
constituted of a unit represented by chemical formula
20 (69) and 0.47 g of 2-amino-1-naphthalenesulfonic acid
were placed in a 100-ml three-necked flask, agitated
with 15.0 ml of pyridine, further added with 1.10 ml of

triphenyl phosphite and heated for 6 hours at 120°C. After the reaction, the polymer was recovered by a re-precipitation in 150 ml of ethanol. The obtained polymer was washed with 1N hydrochloric acid for 1 day, 5 then washed by an agitation in water for 1 day and dried under a reduced pressure to obtain 0.37 g of a polymer. The structure of the obtained polymer was analyzed by ^1H -NMR (FT-NMR: Bruker DPX 400, resonance frequency: 400 MHz, measured species: ^1H , solvent: 10 deuterized DMSO, temperature: room temperature) and a Fourier transformed infrared absorption (FT-IR) spectrum (Nicolet AVATAR 360FT-IR). The IR measurement showed a decrease of a peak at 1695 cm^{-1} attributable to a carboxylic acid, and a new peak at 1658 cm^{-1} 15 attributable to an amide group.

A result of ^1H -NMR confirmed, by a shift in a peak resulting from an aromatic ring of the 2-amino-1-naphthalenesulfonic acid structure, that the polymer was a polyhydroxyalkanoate containing units represented 20 by chemical formula (86) as monomer units.

[0397]

[Chemical Formula 140]



[0398]

It was also confirmed that a proportion of the units of the polyhydroxyalkanoate represented by chemical formula (86) was a copolymer as unit E by 8 mol% and unit F by 92 mol%. An average molecular weight of the obtained polymer was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8120, column: Polymer Laboratories PLgel 5 μ MIXED-C, solvent: DMF/LiBr 0.1 % (w/v), converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 11,000$ and a weight-averaged molecular weight $M_w = 16,600$.

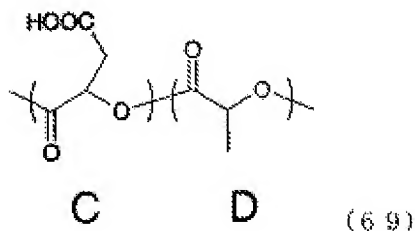
[0399]

15 (Example 42)

Condensation reaction of a polyhydroxyalkanoate constituted of a unit represented by chemical formula (69) synthesized in Example 24 with 1-naphthylamine-8-sulfonic acid

[0400]

[Chemical Formula 141]



[0401]

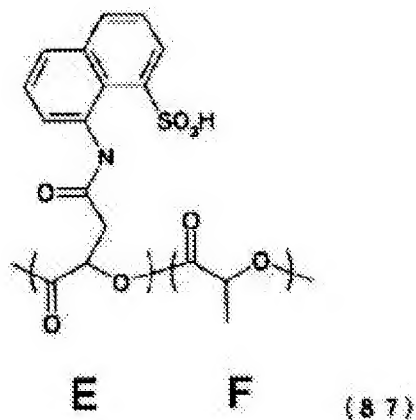
5 In a nitrogen atmosphere, 0.40 g of polymer
synthesized with polyhydroxyalkanoate copolymer (C: 8
mol%, D: 92 mol%) obtained in Example 24 and
constituted of a unit represented by chemical formula
(69) and 0.47 g of 1-naphthylamine-8-sulfonic acid were
10 placed in a 100-ml three-necked flask, agitated with
15.0 ml of pyridine, further added with 1.10 ml of
triphenyl phosphite and heated for 6 hours at 120°C.
After the reaction, the polymer was recovered by a re-
precipitation in 150 ml of ethanol. The obtained
15 polymer was washed with 1N hydrochloric acid for 1 day,
then washed by an agitation in water for 1 day and
dried under a reduced pressure to obtain 0.36 g of a
polymer. The structure of the obtained polymer was
analyzed by ¹H-NMR (FT-NMR: Bruker DPX 400, resonance
20 frequency: 400 MHz, measured species: ¹H, solvent:
deuterized DMSO, temperature: room temperature) and a
Fourier transformed infrared absorption (FT-IR)
spectrum (Nicolet AVATAR 360FT-IR). The IR measurement

showed a decrease of a peak at 1695 cm^{-1} attributable to a carboxylic acid, and a new peak at 1658 cm^{-1} attributable to an amide group.

A result of $^1\text{H-NMR}$ confirmed, by a shift in a peak
5 resulting from an aromatic ring of the 1-naphthylamine-8-sulfonic acid structure, that the polymer was a polyhydroxyalkanoate containing units represented by chemical formula (87) as monomer units.

[0402]

10 [Chemical Formula 142]



[0403]

It was also confirmed that a proportion of the units of the polyhydroxyalkanoate represented by
15 chemical formula (87) was a copolymer as unit E by 8 mol% and unit F by 92 mol%. An average molecular weight of the obtained polymer was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8120, column: Polymer Laboratories PLgel 5μ MIXED-C, solvent:

DMF/LiBr 0.1 %(w/v), converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 10,900$ and a weight-averaged molecular weight $M_w = 17,100$.

5 [0404]

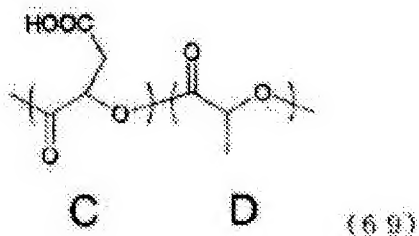
(Example 43)

Condensation reaction of a polyhydroxyalkanoate constituted of a unit represented by chemical formula (69) synthesized in Example 24 with 2-amino-2-methylpropanesulfonic acid

10 methylpropanesulfonic acid

[0405]

[Chemical Formula 143]



[0406]

15 In a nitrogen atmosphere, 0.40 g of polymer synthesized with polyhydroxyalkanoate copolymer (C: 8 mol%, D: 92 mol%) obtained in Example 24 and constituted of a unit represented by chemical formula (69) and 0.32 g of 2-amino-2-methylpropanesulfonic acid

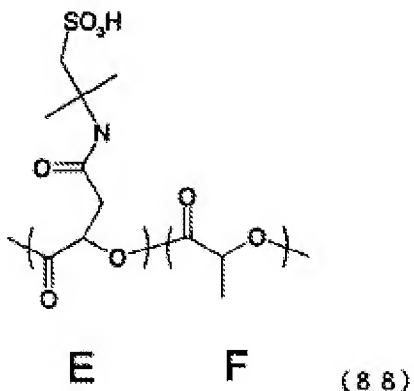
20 were placed in a 100-ml three-necked flask, agitated with 15.0 ml of pyridine, further added with 1.10 ml of triphenyl phosphite and heated for 6 hours at 120°C.

After the reaction, the polymer was recovered by a re-precipitation in 150 ml of ethanol. The obtained polymer was washed with 1N hydrochloric acid for 1 day, then washed by an agitation in water for 1 day and
5 dried under a reduced pressure to obtain 0.33 g of a polymer. The structure of the obtained polymer was analyzed by ^1H -NMR (FT-NMR: Bruker DPX 400, resonance frequency: 400 MHz, measured species: ^1H , solvent: deuterized DMSO, temperature: room temperature) and a
10 Fourier transformed infrared absorption (FT-IR) spectrum (Nicolet AVATAR 360FT-IR). The IR measurement showed a decrease of a peak at 1695 cm^{-1} attributable to a carboxylic acid, and a new peak at 1658 cm^{-1} attributable to an amide group.

15 A result of ^1H -NMR confirmed, by a shift in a peak resulting from an aromatic ring of the 2-amino-2-methylpropanesulfonic acid structure, that the polymer was a polyhydroxyalkanoate containing units represented by chemical formula (88) as monomer units.

20 [0407]

[Chemical Formula 144]



[0408]

It was also confirmed that a proportion of the units of the polyhydroxyalkanoate represented by chemical formula (88) was a copolymer as unit E by 8 mol% and unit F by 92 mol%. An average molecular weight of the obtained polymer was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8120, column: Polymer Laboratories PLgel 5 μ MIXED-C, solvent: DMF/LiBr 0.1 % (w/v), converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 10,300$ and a weight-averaged molecular weight $M_w = 14,700$.

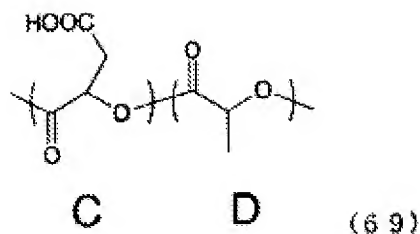
[0409]

(Example 44)

Condensation reaction of a polyhydroxyalkanoate constituted of a unit represented by chemical formula (44) synthesized in Example 24 with taurine

[0410]

[Chemical Formula 145]



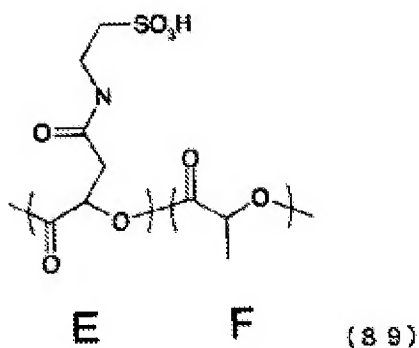
[0411]

In a nitrogen atmosphere, 0.40 g of polymer synthesized with polyhydroxyalkanoate copolymer (C: 8
5 mol%, D: 92 mol%) obtained in Example 24 and constituted of a unit represented by chemical formula (69) and 0.26 g of taurine were placed in a 100-ml three-necked flask, agitated with 15.0 ml of pyridine, further added with 1.10 ml of triphenyl phosphite and
10 heated for 6 hours at 120°C. After the reaction, the polymer was recovered by a re-precipitation in 150 ml of ethanol. The obtained polymer was washed with 1N hydrochloric acid for 1 day, then washed by an agitation in water for 1 day and dried under a reduced
15 pressure to obtain 0.33 g of a polymer. The structure of the obtained polymer was analyzed by ¹H-NMR (FT-NMR: Bruker DPX 400, resonance frequency: 400 MHz, measured species: ¹H, solvent: deuterized DMSO, temperature: room temperature) and a Fourier transformed infrared
20 absorption (FT-IR) spectrum (Nicolet AVATAR 360FT-IR). The IR measurement showed a decrease of a peak at 1695 cm⁻¹ attributable to a carboxylic acid, and a new peak at 1658 cm⁻¹ attributable to an amide group.

A result of ^1H -NMR confirmed, by a shift in a peak resulting from a methylene of the taurine structure, that the polymer was a polyhydroxyalkanoate containing units represented by chemical formula (89) as monomer units.

[0412]

[Chemical Formula 146]



[0413]

It was also confirmed that a proportion of the units of the polyhydroxyalkanoate represented by chemical formula (89) was a copolymer as unit E by 8 mol% and unit F by 92 mol%. An average molecular weight of the obtained polymer was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8120, column: Polymer Laboratories PLgel 5 μ MIXED-C, solvent: DMF/LiBr 0.1 % (w/v), converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 9,900$ and a weight-averaged molecular weight $M_w = 14,100$.

[0414]

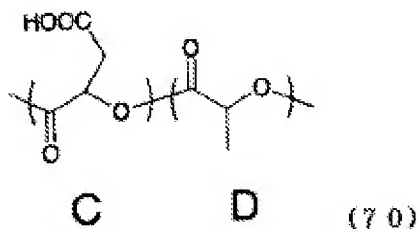
(Example 45)

Condensation reaction of a polyhydroxyalkanoate constituted of a unit represented by chemical formula (70) synthesized in Example 25 with 2-

5 aminobenzenesulfonic acid

[0415]

[Chemical Formula 147]



[0416]

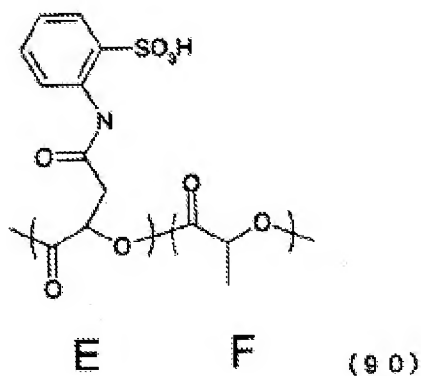
10 In a nitrogen atmosphere, 0.40 g of polymer synthesized with polyhydroxyalkanoate copolymer (C: 4 mol%, D: 96 mol%) obtained in Example 25 and constituted of a unit represented by chemical formula (70) and 0.18 g of 2-aminobenzenesulfonic acid were
15 placed in a 100-ml three-necked flask, agitated with 15.0 ml of pyridine, further added with 0.57 ml of triphenyl phosphite and heated for 6 hours at 120°C. After the reaction, the polymer was recovered by a re-precipitation in 150 ml of ethanol. The obtained
20 polymer was washed with 1N hydrochloric acid for 1 day, then washed by an agitation in water for 1 day and dried under a reduced pressure to obtain 0.32 g of a

polymer. The structure of the obtained polymer was analyzed by ^1H -NMR (FT-NMR: Bruker DPX 400, resonance frequency: 400 MHz, measured species: ^1H , solvent: deuterized DMSO, temperature: room temperature) and a Fourier transformed infrared absorption (FT-IR) spectrum (Nicolet AVATAR 360FT-IR). The IR measurement showed a decrease of a peak at 1695 cm^{-1} attributable to a carboxylic acid, and a new peak at 1658 cm^{-1} attributable to an amide group.

A result of ^1H -NMR confirmed, by a shift in a peak resulting from an aromatic ring of the 2-aminobenzenesulfonic acid structure, that the polymer was a polyhydroxyalkanoate containing units represented by chemical formula (90) as monomer units.

[0417]

[Chemical Formula 148]



[0418]

It was also confirmed that a proportion of the units of the polyhydroxyalkanoate represented by chemical formula (90) was a copolymer as unit E by 4

mol% and unit F by 96 mol%. An average molecular weight of the obtained polymer was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8120, column: Polymer Laboratories PLgel 5 μ MIXED-C, solvent:

5 DMF/LiBr 0.1 %(w/v), converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 12,000$ and a weight-averaged molecular weight $M_w = 15,800$.

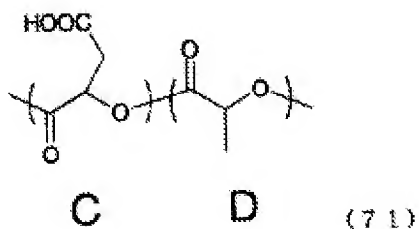
[0419]

10 (Example 46)

Condensation reaction of a polyhydroxyalkanoate constituted of a unit represented by chemical formula (71) synthesized in Example 26 with 2-aminobenzenesulfonic acid

15 [0420]

[Chemical Formula 149]



[0421]

In a nitrogen atmosphere, 0.40 g of polymer
20 synthesized with polyhydroxyalkanoate copolymer (C: 13 mol%, D: 87 mol%) obtained in Example 25 and constituted of a unit represented by chemical formula

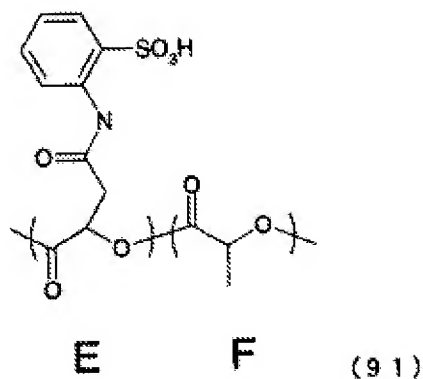
(71) and 0.58 g of 2-aminobenzenesulfonic acid were placed in a 100-ml three-necked flask, agitated with 15.0 ml of pyridine, further added with 1.74 ml of triphenyl phosphite and heated for 6 hours at 120°C.

5 After the reaction, the polymer was recovered by a re-precipitation in 150 ml of ethanol. The obtained polymer was washed with 1N hydrochloric acid for 1 day, then washed by an agitation in water for 1 day and dried under a reduced pressure to obtain 0.32 g of a
10 polymer. The structure of the obtained polymer was analyzed by ^1H -NMR (FT-NMR: Bruker DPX 400, resonance frequency: 400 MHz, measured species: ^1H , solvent: deuterized DMSO, temperature: room temperature) and a Fourier transformed infrared absorption (FT-IR)
15 spectrum (Nicolet AVATAR 360FT-IR). The IR measurement showed a decrease of a peak at 1695 cm^{-1} attributable to a carboxylic acid, and a new peak at 1658 cm^{-1} attributable to an amide group.

A result of ^1H -NMR confirmed, by a shift in a peak
20 resulting from an aromatic ring of the 2-aminobenzenesulfonic acid structure, that the polymer was a polyhydroxyalkanoate containing units represented by chemical formula (91) as monomer units.

[0422]

25 [Chemical Formula 150]



[0423]

It was also confirmed that a proportion of the units of the polyhydroxyalkanoate represented by chemical formula (91) was a copolymer as unit E by 13 mol% and unit F by 87 mol%. An average molecular weight of the obtained polymer was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8120, column: Polymer Laboratories PLgel 5 μ MIXED-C, solvent: DMF/LiBr 0.1 % (w/v), converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 9,500$ and a weight-averaged molecular weight $M_w = 12,600$.

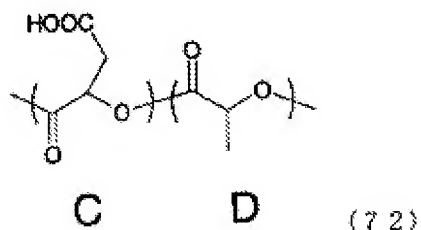
[0424]

15 (Example 47)

Condensation reaction of a polyhydroxyalkanoate constituted of a unit represented by chemical formula (72) synthesized in Example 27 with 2-aminobenzenesulfonic acid

20 [0425]

[Chemical Formula 151]



[0426]

In a nitrogen atmosphere, 0.40 g of polymer
5 synthesized with polyhydroxyalkanoate copolymer (C: 16
mol%, D: 84 mol%) obtained in Example 27 and
constituted of a unit represented by chemical formula
(72) and 0.70 g of 2-aminobenzenesulfonic acid were
placed in a 100-ml three-necked flask, agitated with
10 15.0 ml of pyridine, further added with 2.11 ml of
triphenyl phosphite and heated for 6 hours at 120°C.
After the reaction, the polymer was recovered by a re-
precipitation in 150 ml of ethanol. The obtained
polymer was washed with 1N hydrochloric acid for 1 day,
15 then washed by an agitation in water for 1 day and
dried under a reduced pressure to obtain 0.32 g of a
polymer.

[0427]

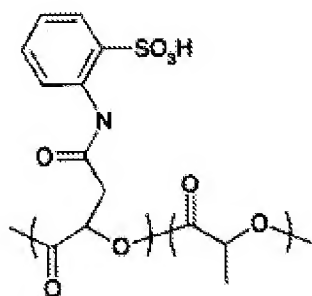
The structure of the obtained polymer was analyzed
20 by ¹H-NMR (FT-NMR: Bruker DPX 400, resonance frequency:
400 MHz, measured species: ¹H, solvent: deuterized
DMSO, temperature: room temperature) and a Fourier
transformed infrared absorption (FT-IR) spectrum

(Nicolet AVATAR 360FT-IR). The IR measurement showed a decrease of a peak at 1695 cm^{-1} attributable to a carboxylic acid, and a new peak at 1658 cm^{-1} attributable to an amide group.

5 A result of ^1H -NMR confirmed, by a shift in a peak resulting from an aromatic ring of the 2-aminobenzenesulfonic acid structure, that the polymer was a polyhydroxyalkanoate containing units represented by chemical formula (92) as monomer units.

10 [0428]

[Chemical Formula 152]



E F (92)

[0429]

15 It was also confirmed that a proportion of the units of the polyhydroxyalkanoate represented by chemical formula (92) was a copolymer as unit E by 16 mol% and unit F by 84 mol%. An average molecular weight of the obtained polymer was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8120, column: 20 Polymer Laboratories PLgel 5μ MIXED-C, solvent:

DMF/LiBr 0.1 % (w/v), converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 9,100$ and a weight-averaged molecular weight $M_w = 12,200$.

5 [0430]

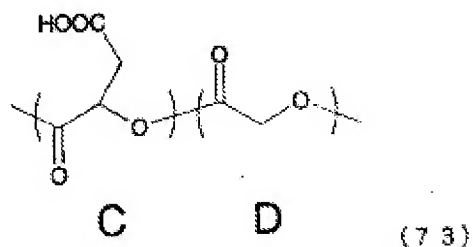
(Example 48)

Condensation reaction of a polyhydroxyalkanoate constituted of a unit represented by chemical formula (73) synthesized in Example 28 with 2-

10 aminobenzenesulfonic acid

[0431]

[Chemical Formula 153]



[0432]

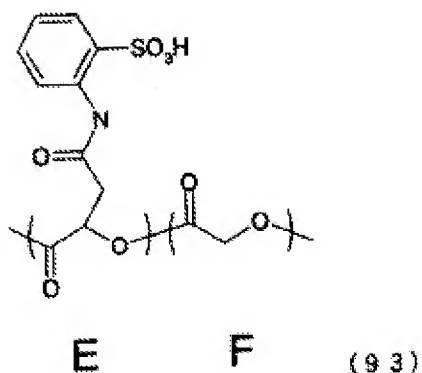
15 In a nitrogen atmosphere, 0.40 g of polymer synthesized with polyhydroxyalkanoate copolymer (C: 9 mol%, D: 91 mol%) obtained in Example 28 and constituted of a unit represented by chemical formula (73) and 0.49 g of 2-aminobenzenesulfonic acid were
20 placed in a 100-ml three-necked flask, agitated with 15.0 ml of pyridine, further added with 1.48 ml of triphenyl phosphite and heated for 6 hours at 120°C.

After the reaction, the polymer was recovered by a re-precipitation in 150 ml of ethanol. The obtained polymer was washed with 1N hydrochloric acid for 1 day, then washed by an agitation in water for 1 day and
5 dried under a reduced pressure to obtain 0.35 g of a polymer. The structure of the obtained polymer was analyzed by ^1H -NMR (FT-NMR: Bruker DPX 400, resonance frequency: 400 MHz, measured species: ^1H , solvent: deuterized DMSO, temperature: room temperature) and a
10 Fourier transformed infrared absorption (FT-IR) spectrum (Nicolet AVATAR 360FT-IR). The IR measurement showed a decrease of a peak at 1695 cm^{-1} attributable to a carboxylic acid, and a new peak at 1658 cm^{-1} attributable to an amide group.

15 A result of ^1H -NMR confirmed, by a shift in a peak resulting from an aromatic ring of the 2-aminobenzenesulfonic acid structure, that the polymer was a polyhydroxyalkanoate containing units represented by chemical formula (93) as monomer units.

20 [0433]

[Chemical Formula 154]



[0434]

It was also confirmed that a proportion of the units of the polyhydroxyalkanoate represented by chemical formula (93) was a copolymer as unit E by 9 mol% and unit F by 91 mol%. An average molecular weight of the obtained polymer was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8120, column: Polymer Laboratories PLgel 5 μ MIXED-C, solvent: DMF/LiBr 0.1 % (w/v), converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 11,900$ and a weight-averaged molecular weight $M_w = 16,200$.

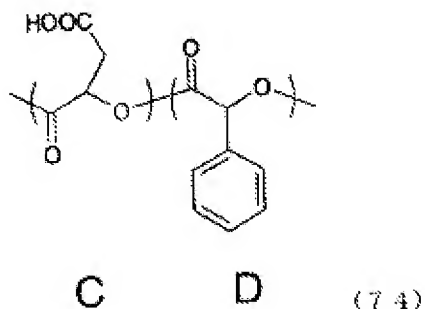
[0435]

15 (Example 49)

Condensation reaction of a polyhydroxyalkanoate constituted of a unit represented by chemical formula (74) synthesized in Example 29 with 2-aminobenzenesulfonic acid

20 [0436]

[Chemical Formula 155]



[0437]

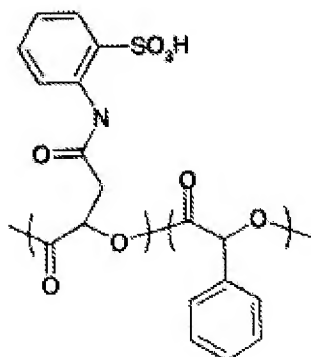
In a nitrogen atmosphere, 0.40 g of polymer
5 synthesized with polyhydroxyalkanoate copolymer (C: 7
mol%, D: 93 mol%) obtained in Example 29 and
constituted of a unit represented by chemical formula
(74) and 0.18 g of 2-aminobenzenesulfonic acid were
placed in a 100-ml three-necked flask, agitated with
10 15.0 ml of pyridine, further added with 0.55 ml of
triphenyl phosphite and heated for 6 hours at 120°C.
After the reaction, the polymer was recovered by a re-
precipitation in 150 ml of ethanol. The obtained
polymer was washed with 1N hydrochloric acid for 1 day,
15 then washed by an agitation in water for 1 day and
dried under a reduced pressure to obtain 0.34 g of a
polymer. The structure of the obtained polymer was
analyzed by ¹H-NMR (FT-NMR: Bruker DPX 400, resonance
frequency: 400 MHz, measured species: ¹H, solvent:
20 deuterized DMSO, temperature: room temperature) and a
Fourier transformed infrared absorption (FT-IR)

spectrum (Nicolet AVATAR 360FT-IR). The IR measurement showed a decrease of a peak at 1695 cm^{-1} attributable to a carboxylic acid, and a new peak at 1658 cm^{-1} attributable to an amide group.

5 A result of ^1H -NMR confirmed, by a shift in a peak resulting from an aromatic ring of the 2-aminobenzenesulfonic acid structure, that the polymer was a polyhydroxyalkanoate containing units represented by chemical formula (94) as monomer units.

10 [0438]

[Chemical Formula 156]



E F (94)

[0439]

15 It was also confirmed that a proportion of the units of the polyhydroxyalkanoate represented by chemical formula (94) was a copolymer as unit E by 7 mol% and unit F by 93 mol%. An average molecular weight of the obtained polymer was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8120, column:

Polymer Laboratories PLgel 5 μ MIXED-C, solvent:
DMF/LiBr 0.1 %(w/v), converted as polystyrene). As a
result, there were obtained a number-averaged molecular
weight $M_n = 11,400$ and a weight-averaged molecular
weight $M_w = 23,100$.

[0440]

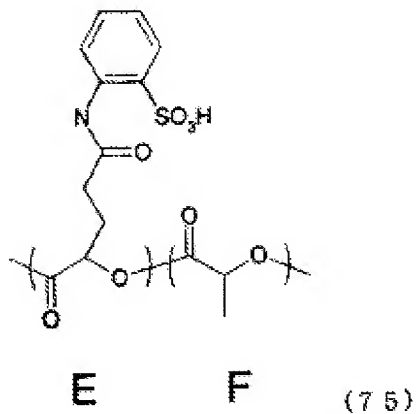
(Example 50)

Esterification reaction of a polyhydroxyalkanoate
constituted of a unit represented by chemical formula

(75) synthesized in Example 30

[0441]

[Chemical Formula 157]



[0442]

0.30 g of polyhydroxyalkanoate copolymer (E: 8
mol%, F: 92 mol%) obtained in Example 30 and
constituted of a unit represented by chemical formula
(75) were placed in an eggplant-shaped flask, dissolved
by adding 21.0 ml of chloroform and 7.0 ml of methanol,

and cooled to 0°C. Then 1.35 ml of a 2 mol/L hexane solution of trimethylsilyl diazomethane (manufactured by Aldrich Inc.) were added and the mixture was agitated for 4 hours. After the reaction, the solvent was distilled off in an evaporator to recover a polymer.

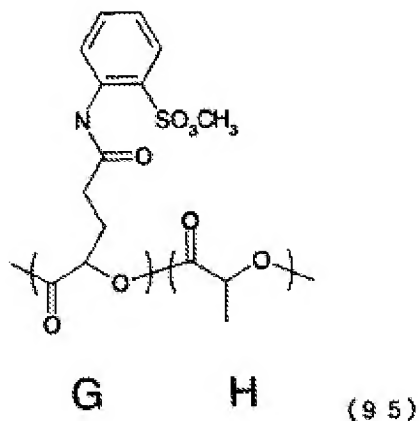
The polymer was re-dissolved by adding 21.0 ml of chloroform and 7.0 ml of methanol, and the solvent was distilled off in an evaporator. This process was repeated three times. The recovered polymer was dried under a reduced pressure to obtain 0.30 g of a polymer. The structure of the obtained polymer was analyzed by ¹H-NMR (FT-NMR: Bruker DPX 400, resonance frequency: 400 MHz, measured species: ¹H, solvent: deuterized DMSO, temperature: room temperature).

[0443]

A result of ¹H-NMR confirmed, based on a peak attributable to methyl sulfonate at 3 - 4 ppm, that the polymer was a polyhydroxyalkanoate containing units represented by chemical formula (95) as monomer units.

[0444]

[Chemical Formula 158]



[0445]

It was also confirmed that a proportion of the units of the polyhydroxyalkanoate represented by chemical formula (95) was a copolymer as unit G by 8 mol% and unit H by 92 mol%. Also an acid value titration utilizing a potentiometric titration apparatus AT510 (manufactured by Kyoto Electron Co.) did not show a peak attributable to a sulfonic acid, thus clarifying that the sulfonic acid was converted to methyl sulfonate. An average molecular weight of the obtained polymer was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8120, column: Polymer Laboratories PLgel 5 μ MIXED-C, solvent: DMF/LiBr 0.1 % (w/v), converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 10,900$ and a weight-averaged molecular weight $M_w = 15,600$.

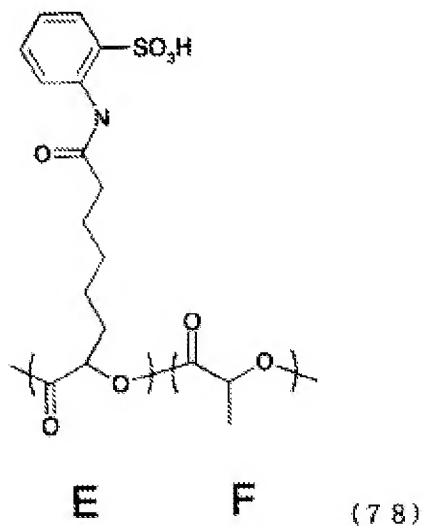
[0446]

(Example 51)

Esterification reaction of a polyhydroxyalkanoate constituted of a unit represented by chemical formula (78) synthesized in Example 33

[0447]

5 [Chemical Formula 159]



[0448]

0.30 g of polyhydroxyalkanoate copolymer (E: 7 mol%, F: 93 mol%) obtained in Example 33 and constituted of a unit represented by chemical formula (78) were placed in an eggplant-shaped flask, dissolved by adding 21.0 ml of chloroform and 7.0 ml of methanol, and cooled to 0°C. Then 1.17 ml of a 2 mol/L hexane solution of trimethylsilyl diazomethane (manufactured by Aldrich Inc.) were added and the mixture was agitated for 4 hours. After the reaction, the solvent was distilled off in an evaporator to recover a polymer.

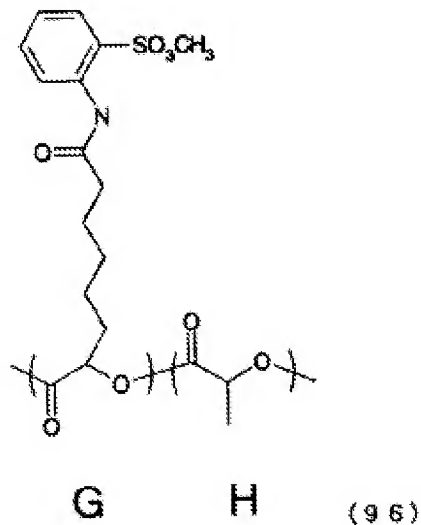
The polymer was re-dissolved by adding 21.0 ml of chloroform and 7.0 ml of methanol, and the solvent was distilled off in an evaporator. This process was repeated three times. The recovered polymer was dried under a reduced pressure to obtain 0.30 g of a polymer. The structure of the obtained polymer was analyzed by ¹H-NMR (FT-NMR: Bruker DPX 400, resonance frequency: 400 MHz, measured species: ¹H, solvent: deuterized DMSO, temperature: room temperature).

10 [0449]

A result of ¹H-NMR confirmed, based on a peak attributable to methyl sulfonate at 3 - 4 ppm, that the polymer was a polyhydroxyalkanoate containing units represented by chemical formula (96) as monomer units.

15 [0450]

[Chemical Formula 160]



[0451]

It was also confirmed that a proportion of the units of the polyhydroxyalkanoate represented by chemical formula (96) was a copolymer as unit G by 7
5 mol% and unit H by 93 mol%.

[0452]

Also an acid value titration utilizing a potentiometric titration apparatus AT510 (manufactured by Kyoto Electron Co.) did not show a peak attributable
10 to a sulfonic acid, thus clarifying that the sulfonic acid was converted to methyl sulfonate. An average molecular weight of the obtained polymer was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8120, column: Polymer Laboratories PLgel 5 μ MIXED-C, solvent:
15 DMF/LiBr 0.1 %(w/v), converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 9,700$ and a weight-averaged molecular weight $M_w = 13,800$.

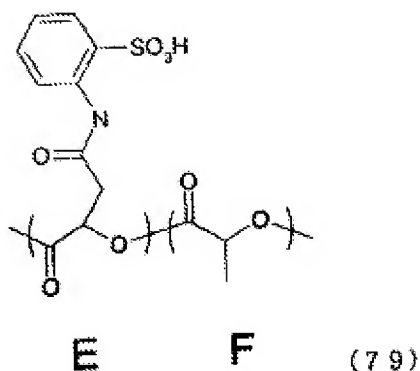
[0453]

20 (Example 52)

Esterification reaction of a polyhydroxyalkanoate constituted of a unit represented by chemical formula (79) synthesized in Example 34

[0454]

25 [Chemical Formula 161]



[0455]

0.30 g of polyhydroxyalkanoate copolymer (E: 8 mol%, F: 92 mol%) obtained in Example 34 and constituted of a unit represented by chemical formula (79) were placed in an eggplant-shaped flask, dissolved by adding 21.0 ml of chloroform and 7.0 ml of methanol, and cooled to 0°C. Then 1.36 ml of a 2 mol/L hexane solution of trimethylsilyl diazomethane (manufactured by Aldrich Inc.) were added and the mixture was agitated for 4 hours. After the reaction, the solvent was distilled off in an evaporator to recover a polymer.

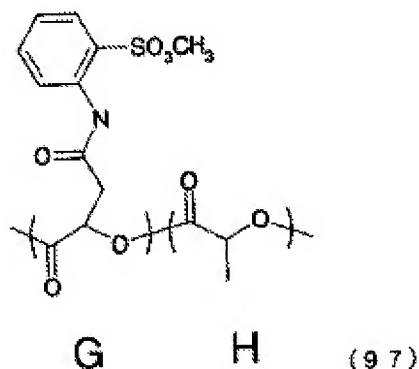
[0456]

The polymer was re-dissolved by adding 21.0 ml of chloroform and 7.0 ml of methanol, and the solvent was distilled off in an evaporator. This process was repeated three times. The recovered polymer was dried under a reduced pressure to obtain 0.31 g of a polymer. The structure of the obtained polymer was analyzed by

^1H -NMR (FT-NMR: Bruker DPX 400, resonance frequency:
400 MHz, measured species: ^1H , solvent: deuterized
DMSO, temperature: room temperature). A result of ^1H -
NMR confirmed, based on a peak attributable to methyl
5 sulfonate at 3 - 4 ppm, that the polymer was a
polyhydroxyalkanoate containing units represented by
chemical formula (97) as monomer units.

[0457]

[Chemical Formula 162]



10

[0458]

It was also confirmed that a proportion of the
units of the polyhydroxyalkanoate represented by
chemical formula (97) was a copolymer as unit G by 8
15 mol% and unit H by 92 mol%. Also an acid value
titration utilizing a potentiometric titration
apparatus AT510 (manufactured by Kyoto Electron Co.)
did not show a peak attributable to a sulfonic acid,
thus clarifying that the sulfonic acid was converted to
20 methyl sulfonate. An average molecular weight of the

obtained polymer was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8120, column: Polymer Laboratories PLgel 5 μ MIXED-C, solvent: DMF/LiBr 0.1 % (w/v), converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 11,600$ and a weight-averaged molecular weight $M_w = 16,900$.

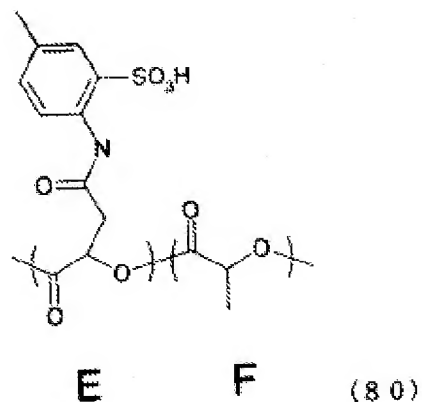
[0459]

(Example 53)

10 Esterification reaction of a polyhydroxyalkanoate constituted of a unit represented by chemical formula (80) synthesized in Example 35

[0460]

[Chemical Formula 163]



15

[0461]

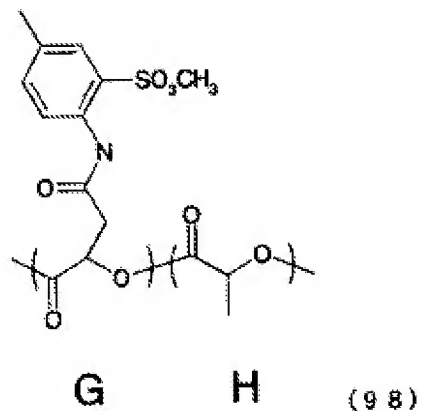
0.30 g of polyhydroxyalkanoate copolymer (E: 8 mol%, F: 92 mol%) obtained in Example 35 and constituted of a unit represented by chemical formula (80) were placed in an eggplant-shaped flask, dissolved

20

by adding 21.0 ml of chloroform and 7.0 ml of methanol,
and cooled to 0°C. Then 1.35 ml of a 2 mol/L hexane
solution of trimethylsilyl diazomethane (manufactured
by Aldrich Inc.) were added and the mixture was
5 agitated for 4 hours. After the reaction, the solvent
was distilled off in an evaporator to recover a
polymer. The polymer was re-dissolved by adding 21.0
ml of chloroform and 7.0 ml of methanol, and the
solvent was distilled off in an evaporator. This
10 process was repeated three times. The recovered
polymer was dried under a reduced pressure to obtain
0.30 g of a polymer. The structure of the obtained
polymer was analyzed by ¹H-NMR (FT-NMR: Bruker DPX 400,
resonance frequency: 400 MHz, measured species: ¹H,
15 solvent: deuterized DMSO, temperature: room
temperature). A result of ¹H-NMR confirmed, based on a
peak attributable to methyl sulfonate at 3 - 4 ppm,
that the polymer was a polyhydroxyalkanoate containing
units represented by chemical formula (98) as monomer
20 units.

[0462]

[Chemical Formula 164]



[0463]

It was also confirmed that a proportion of the units of the polyhydroxyalkanoate represented by chemical formula (98) was a copolymer as unit G by 8 mol% and unit H by 92 mol%. Also an acid value titration utilizing a potentiometric titration apparatus AT510 (manufactured by Kyoto Electron Co.) did not show a peak attributable to a sulfonic acid, thus clarifying that the sulfonic acid was converted to methyl sulfonate. An average molecular weight of the obtained polymer was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8120, column: Polymer Laboratories PLgel 5 μ MIXED-C, solvent: DMF/LiBr 0.1 % (w/v), converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 10,500$ and a weight-averaged molecular weight $M_w = 15,500$.

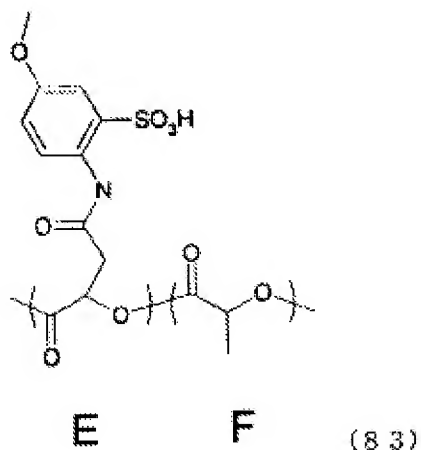
[0464]

20 (Example 54)

Esterification reaction of a polyhydroxyalkanoate constituted of a unit represented by chemical formula (83) synthesized in Example 38

[0465]

5 [Chemical Formula 165]



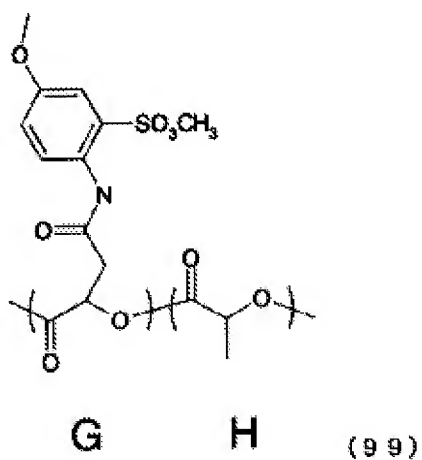
[0466]

0.30 g of polyhydroxyalkanoate copolymer (E: 8 mol%, F: 92 mol%) obtained in Example 38 and
10 constituted of a unit represented by chemical formula (83) were placed in an eggplant-shaped flask, dissolved by adding 21.0 ml of chloroform and 7.0 ml of methanol, and cooled to 0°C. Then 1.33 ml of a 2 mol/L hexane solution of trimethylsilyl diazomethane (manufactured
15 by Aldrich Inc.) were added and the mixture was agitated for 4 hours. After the reaction, the solvent was distilled off in an evaporator to recover a polymer. The polymer was re-dissolved by adding 21.0 ml of chloroform and 7.0 ml of methanol, and the

solvent was distilled off in an evaporator. This process was repeated three times. The recovered polymer was dried under a reduced pressure to obtain 0.30 g of a polymer. The structure of the obtained
5 polymer was analyzed by ^1H -NMR (FT-NMR: Bruker DPX 400, resonance frequency: 400 MHz, measured species: ^1H , solvent: deuterized DMSO, temperature: room temperature). A result of ^1H -NMR confirmed, based on a peak attributable to methyl sulfonate at 3 - 4 ppm,
10 that the polymer was a polyhydroxyalkanoate containing units represented by chemical formula (99) as monomer units.

[0467]

[Chemical Formula 166]



15

[0468]

It was also confirmed that a proportion of the units of the polyhydroxyalkanoate represented by

chemical formula (99) was a copolymer as unit G by 8 mol% and unit H by 92 mol%. Also an acid value titration utilizing a potentiometric titration apparatus AT510 (manufactured by Kyoto Electron Co.)
5 did not show a peak attributable to a sulfonic acid, thus clarifying that the sulfonic acid was converted to methyl sulfonate. An average molecular weight of the obtained polymer was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8120, column: Polymer
10 Laboratories PLgel 5 μ MIXED-C, solvent: DMF/LiBr 0.1 % (w/v), converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 10,700$ and a weight-averaged molecular weight $M_w = 15,900$.

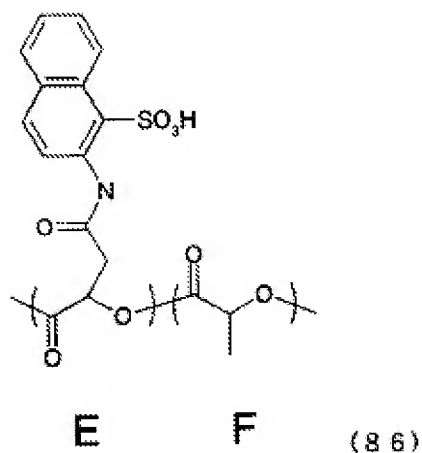
15 [0469]

(Example 55)

Esterification reaction of a polyhydroxyalkanoate constituted of a unit represented by chemical formula (86) synthesized in Example 41

20 [0470]

[Chemical Formula 167]



[0471]

0.30 g of polyhydroxyalkanoate copolymer (E: 8 mol%, F: 92 mol%) obtained in Example 43 and constituted of a unit represented by chemical formula (86) were placed in an eggplant-shaped flask, dissolved by adding 21.0 ml of chloroform and 7.0 ml of methanol, and cooled to 0°C. Then 1.30 ml of a 2 mol/L hexane solution of trimethylsilyl diazomethane (manufactured by Aldrich Inc.) were added and the mixture was agitated for 4 hours. After the reaction, the solvent was distilled off in an evaporator to recover a polymer. The polymer was re-dissolved by adding 21.0 ml of chloroform and 7.0 ml of methanol, and the solvent was distilled off in an evaporator. This process was repeated three times. The recovered polymer was dried under a reduced pressure to obtain 0.30 g of a polymer. The structure of the obtained

by Kyoto Electron Co.) did not show a peak attributable to a sulfonic acid, thus clarifying that the sulfonic acid was converted to methyl sulfonate. An average molecular weight of the obtained polymer was evaluated
5 by gel permeation chromatography (GPC: Tosoh HLC-8120, column: Polymer Laboratories PLgel 5 μ MIXED-C, solvent: DMF/LiBr 0.1 %(w/v), converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 10,900$ and a weight-averaged molecular
10 weight $M_w = 17,200$.

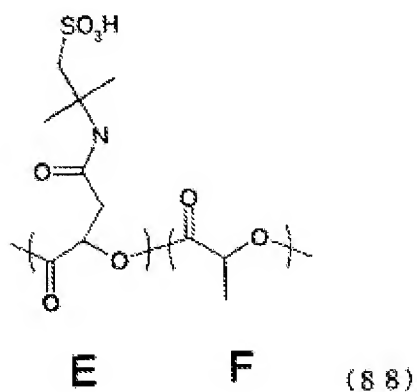
[0475]

(Example 56)

Esterification reaction of a polyhydroxyalkanoate constituted of a unit represented by chemical formula
15 (88) synthesized in Example 43

[0476]

[Chemical Formula 169]



[0477]

20 0.30 g of polyhydroxyalkanoate copolymer (E: 8

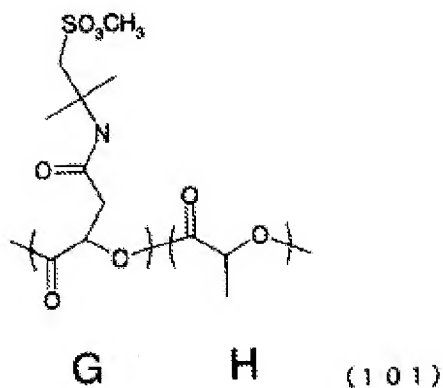
mol%, F: 92 mol%) obtained in Example 43 and constituted of a unit represented by chemical formula (88) were placed in an eggplant-shaped flask, dissolved by adding 21.0 ml of chloroform and 7.0 ml of methanol, and cooled to 0°C. Then 1.39 ml of a 2 mol/L hexane solution of trimethylsilyl diazomethane (manufactured by Aldrich Inc.) were added and the mixture was agitated for 4 hours. After the reaction, the solvent was distilled off in an evaporator to recover a polymer.

[0478]

The polymer was re-dissolved by adding 21.0 ml of chloroform and 7.0 ml of methanol, and the solvent was distilled off in an evaporator. This process was repeated three times. The recovered polymer was dried under a reduced pressure to obtain 0.31 g of a polymer. The structure of the obtained polymer was analyzed by ¹H-NMR (FT-NMR: Bruker DPX 400, resonance frequency: 400 MHz, measured species: ¹H, solvent: deuterized DMSO, temperature: room temperature). A result of ¹H-NMR confirmed, based on a peak attributable to methyl sulfonate at 3 - 4 ppm, that the polymer was a polyhydroxyalkanoate containing units represented by chemical formula (101) as monomer units.

[0479]

[Chemical Formula 170]



[0480]

It was also confirmed that a proportion of the units of the polyhydroxyalkanoate represented by chemical formula (101) was a copolymer as unit G by 8 mol% and unit H by 92 mol%. Also an acid value titration utilizing a potentiometric titration apparatus AT510 (manufactured by Kyoto Electron Co.) did not show a peak attributable to a sulfonic acid, thus clarifying that the sulfonic acid was converted to methyl sulfonate. An average molecular weight of the obtained polymer was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8120, column: Polymer Laboratories PLgel 5 μ MIXED-C, solvent: DMF/LiBr 0.1 % (w/v), converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 9,900$ and a weight-averaged molecular weight $M_w = 14,500$.

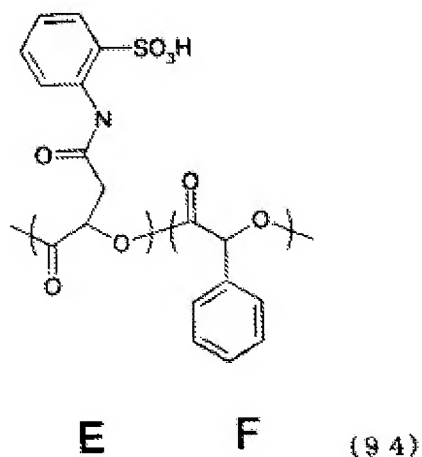
[0481]

(Example 57)

Esterification reaction of a polyhydroxyalkanoate constituted of a unit represented by chemical formula (94) synthesized in Example 49

[0482]

5 [Chemical Formula 171]



[0483]

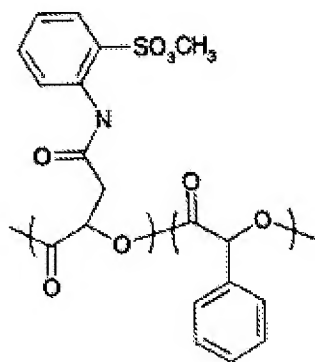
0.30 g of polyhydroxyalkanoate copolymer (E: 7 mol%, F: 93 mol%) obtained in Example 49 and constituted of a unit represented by chemical formula (94) were placed in an eggplant-shaped flask, dissolved by adding 21.0 ml of chloroform and 7.0 ml of methanol, and cooled to 0°C. Then 0.73 ml of a 2 mol/L hexane solution of trimethylsilyl diazomethane (manufactured by Aldrich Inc.) were added and the mixture was agitated for 4 hours. After the reaction, the solvent was distilled off in an evaporator to recover a polymer. The polymer was re-dissolved by adding 21.0 ml of chloroform and 7.0 ml of methanol, and the

10
15

solvent was distilled off in an evaporator. This process was repeated three times. The recovered polymer was dried under a reduced pressure to obtain 0.30 g of a polymer. The structure of the obtained
5 polymer was analyzed by ^1H -NMR (FT-NMR: Bruker DPX 400, resonance frequency: 400 MHz, measured species: ^1H , solvent: deuterized DMSO, temperature: room temperature). A result of ^1H -NMR confirmed, based on a peak attributable to methyl sulfonate at 3 - 4 ppm,
10 that the polymer was a polyhydroxyalkanoate containing units represented by chemical formula (102) as monomer units.

[0484]

[Chemical Formula 172]



G

H

(102)

15

[0485]

It was also confirmed that a proportion of the units of the polyhydroxyalkanoate represented by chemical formula (102) was a copolymer as unit G by 7

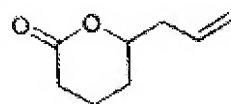
mol% and unit H by 93 mol%. Also an acid value titration utilizing a potentiometric titration apparatus AT510 (manufactured by Kyoto Electron Co.) did not show a peak attributable to a sulfonic acid, thus clarifying that the sulfonic acid was converted to methyl sulfonate. An average molecular weight of the obtained polymer was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8120, column: Polymer Laboratories PLgel 5 μ MIXED-C, solvent: DMF/LiBr 0.1 % (w/v), converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 11,200$ and a weight-averaged molecular weight $M_w = 23,000$.

[0486]

15 (Example 58)

[0487]

[Chemical Formula 173]



(103)

[0488]

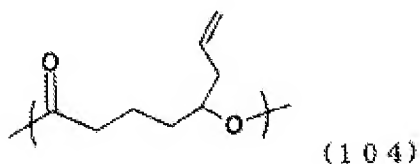
20 [Polyester synthesis utilizing tetrahydro-6-(2-propenyl)-2H-pyran-2-one represented by chemical formula (103)]

1.40 g (10.0 mmol) of tetrahydro-6-(2-propenyl)-2H-pyran-2-one, 20 μ l of a 2M toluene solution of di-

iso-propyl zinc and 8 ml of a 0.01M toluene solution of p-tert-butylbenzyl alcohol were charged in a polymerization ampoule, then subjected to a drying for 1 hour under a reduced pressure and a nitrogen replacement, and the ampoule was sealed by fusing under a reduced pressure and heated at 150°C to execute a ring-opening polymerization. The reaction was terminated after 10 hours and the mixture was cooled. An obtained polymer was dissolved in chloroform, and was re-precipitated in methanol of a 10 times amount of that of chloroform required for dissolving. The precipitate was recovered and dried under a reduced pressure to obtain 0.46 g of a polymer. An NMR analysis conducted under conditions same as in Example 6 for specifying the structure of the obtained polymer confirmed as a polyhydroxyalkanoate constituted of a unit represented by chemical formula (104) as the monomer:

[0489]

20 [Chemical Formula 174]



[0490]

An average molecular weight of the obtained polyhydroxyalkanoate was evaluated by gel permeation

chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-GEL Super HM-H, solvent: chloroform, converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 10,100$ and a weight-averaged molecular weight $M_w = 12,100$.

[0491]

(Example 59)

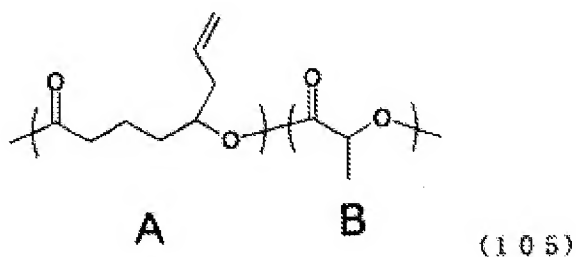
[Polyester synthesis utilizing tetrahydro-6-(2-propenyl)-2H-pyrane-2-one and L-lactide]

0.42 g (3.0 mmol) of tetrahydro-6-(2-propenyl)-2H-pyrane-2-one, 1.01 g (7.0 mmol) of L-lactide, 20 μ l of a 2M toluene solution of di-iso-propyl zinc and 8 ml of a 0.01M toluene solution of p-tert-butylbenzyl alcohol were charged in a polymerization ampoule, then subjected to a drying for 1 hour under a reduced pressure and a nitrogen replacement, and the ampoule was sealed by fusing under a reduced pressure and heated at 150°C to execute a ring-opening polymerization. The reaction was terminated after 10 hours and the mixture was cooled. An obtained polymer was dissolved in chloroform, and was re-precipitated in methanol of a 10 times amount of that of chloroform required for dissolving. The precipitate was recovered and dried under a reduced pressure to obtain 0.84 g of a polymer. An NMR analysis conducted under conditions same as in Example 6 for specifying the structure of the obtained polymer confirmed as a

polyhydroxyalkanoate constituted of a unit represented by chemical formula (105) as the monomer. It was also confirmed that a proportion of the monomer units was unit A by 17 mol% and unit B by 83 mol%:

5 [0492]

[Chemical Formula 175]



[0493]

An average molecular weight of the obtained
10 polyhydroxyalkanoate was evaluated by gel permeation
chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-
GEL Super HM-H, solvent: chloroform, converted as
polystyrene). As a result, there were obtained a
number-averaged molecular weight $M_n = 68,100$ and a
15 weight-averaged molecular weight $M_w = 104,200$.

[0494]

(Example 60)

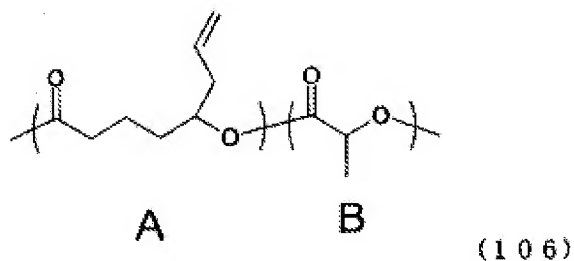
[Polyester synthesis utilizing tetrahydro-6-(2-propenyl)-2H-pyran-2-one and L-lactide]

20 0.28 g (2.0 mmol) of tetrahydro-6-(2-propenyl)-2H-
pyran-2-one, 1.15 g (8.0 mmol) of L-lactide, 20 μ l of
a 2M toluene solution of di-iso-propyl zinc and 8 ml of

a 0.01M toluene solution of p-tert-butylbenzyl alcohol
were charged in a polymerization ampoule, then
subjected to a drying for 1 hour under a reduced
pressure and a nitrogen replacement, and the ampoule
5 was sealed by fusing under a reduced pressure and
heated at 150°C to execute a ring-opening
polymerization. The reaction was terminated after 10
hours and the mixture was cooled. An obtained polymer
was dissolved in chloroform, and was re-precipitated in
10 methanol of a 10 times amount of that of chloroform
required for dissolving. The precipitate was recovered
and dried under a reduced pressure to obtain 1.06 g of
a polymer. An NMR analysis conducted under conditions
same as in Example 6 for specifying the structure of
15 the obtained polymer confirmed as a
polyhydroxyalkanoate constituted of a unit represented
by chemical formula (106) as the monomer. It was also
confirmed that a proportion of the monomer units was
unit A by 11 mol% and unit B by 89 mol%:

20 [0495]

[Chemical Formula 176]



[0496]

An average molecular weight of the obtained polyhydroxyalkanoate was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-
5 GEL Super HM-H, solvent: chloroform, converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 142,500$ and a weight-averaged molecular weight $M_w = 233,700$.

[0497]

10 (Example 61)

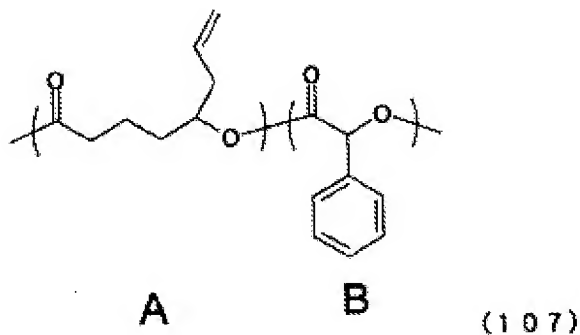
[Polyester synthesis utilizing tetrahydro-6-(2-propenyl)-2H-pyran-2-one and mandelide]

0.28 g (2.0 mmol) of tetrahydro-6-(2-propenyl)-2H-pyran-2-one, 2.15 g (8.0 mmol) of mandelide, 20 μ l of
15 a 2M toluene solution of di-iso-propyl zinc and 8 ml of a 0.01M toluene solution of p-tert-butylbenzyl alcohol were charged in a polymerization ampoule, then subjected to a drying for 1 hour under a reduced pressure and a nitrogen replacement, and the ampoule
20 was sealed by fusing under a reduced pressure and heated at 150°C to execute a ring-opening polymerization. The reaction was terminated after 10 hours and the mixture was cooled. An obtained polymer was dissolved in chloroform, and was re-precipitated in
25 methanol of a 10 times amount of that of chloroform required for dissolving. The precipitate was recovered and dried under a reduced pressure to obtain 1.59 g of

a polymer. An NMR analysis conducted under conditions same as in Example 6 for specifying the structure of the obtained polymer confirmed as a polyhydroxyalkanoate constituted of a unit represented
5 by chemical formula (107) as the monomer. It was also confirmed that a proportion of the monomer units was unit A by 12 mol% and unit B by 88 mol%:

[0498]

[Chemical Formula 177]



10

[0499]

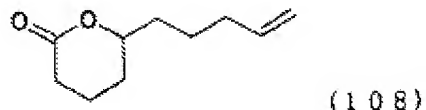
An average molecular weight of the obtained polyhydroxyalkanoate was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-
15 GEL Super HM-H, solvent: chloroform, converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 12,000$ and a weight-averaged molecular weight $M_w = 24,200$.

[0500]

20 (Example 62)

[0501]

[Chemical Formula 178]



[0502]

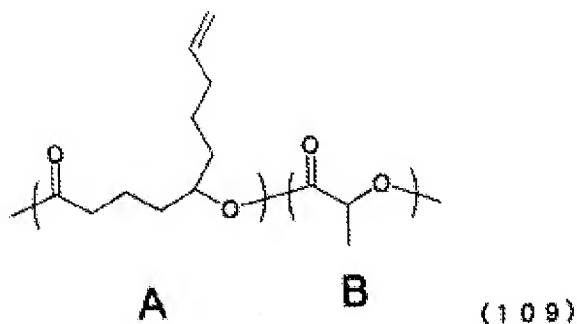
[Polyester synthesis utilizing tetrahydro-6-(4-propenyl)-2H-pyran-2-one represented by chemical formula (108) and L-lactide]

0.34 g (2.0 mmol) of tetrahydro-6-(4-propenyl)-2H-pyran-2-one, 1.15 g (8.0 mmol) of L-lactide, 20 μ l of a 2M toluene solution of di-iso-propyl zinc and 8 ml of a 0.01M toluene solution of p-tert-butylbenzyl alcohol were charged in a polymerization ampoule, then subjected to a drying for 1 hour under a reduced pressure and a nitrogen replacement, and the ampoule was sealed by fusing under a reduced pressure and heated at 150°C to execute a ring-opening polymerization. The reaction was terminated after 10 hours and the mixture was cooled. An obtained polymer was dissolved in chloroform, and was re-precipitated in methanol of a 10 times amount of that of chloroform required for dissolving. The precipitate was recovered and dried under a reduced pressure to obtain 0.89 g of a polymer. An NMR analysis conducted under conditions same as in Example 6 for specifying the structure of the obtained polymer confirmed as a polyhydroxyalkanoate constituted of a unit represented

by chemical formula (109) as the monomer. It was also confirmed that a proportion of the monomer units was unit A by 8 mol% and unit B by 92 mol%:

[0503]

5 [Chemical Formula 179]



[0504]

An average molecular weight of the obtained polyhydroxyalkanoate was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-GEL Super HM-H, solvent: chloroform, converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 49,000$ and a weight-averaged molecular weight $M_w = 88,200$.

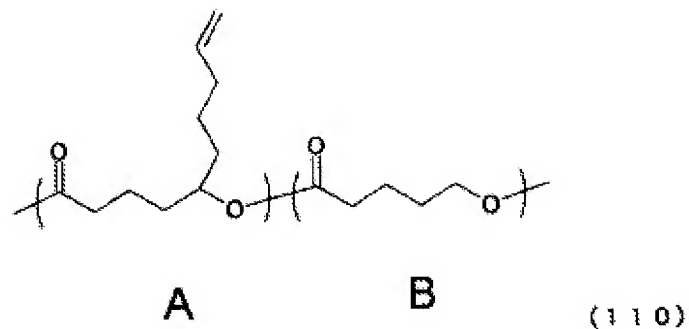
15 [0505]

(Example 63)

[Polyester synthesis utilizing tetrahydro-6-(4-propenyl)-2H-pyran-2-one and δ -valerolactone]

0.34 g (2.0 mmol) of tetrahydro-6-(4-propenyl)-2H-pyran-2-one, 0.80 g (8.0 mmol) of δ -valerolactone, 20 μ l of a 2M toluene solution of di-iso-propyl zinc and 8

ml of a 0.01M toluene solution of p-tert-butylbenzyl
alcohol were charged in a polymerization ampoule, then
subjected to a drying for 1 hour under a reduced
pressure and a nitrogen replacement, and the ampoule
5 was sealed by fusing under a reduced pressure and
heated at 150°C to execute a ring-opening
polymerization. The reaction was terminated after 10
hours and the mixture was cooled. An obtained polymer
was dissolved in chloroform, and was re-precipitated in
10 methanol of a 10 times amount of that of chloroform
required for dissolving. The precipitate was recovered
and dried under a reduced pressure to obtain 0.89 g of
a polymer. An NMR analysis conducted under conditions
same as in Example 6 for specifying the structure of
15 the obtained polymer confirmed as a
polyhydroxyalkanoate constituted of a unit represented
by chemical formula (110) as the monomer. It was also
confirmed that a proportion of the monomer units was
unit A by 8 mol% and unit B by 92 mol%:
20 [0506]
[Chemical Formula 180]



[0507]

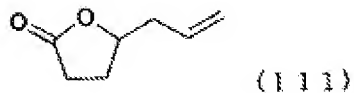
An average molecular weight of the obtained polyhydroxyalkanoate was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-GEL Super HM-H, solvent: chloroform, converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 8,900$ and a weight-averaged molecular weight $M_w = 11,900$.

10 [0508]

(Example 64)

[0509]

[Chemical Formula 181]



15 [0510]

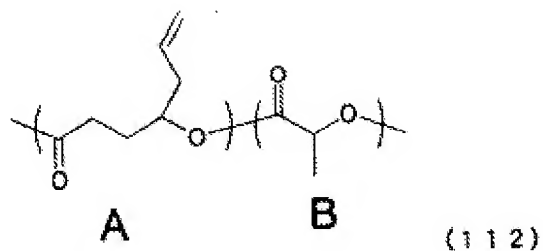
[Polyester synthesis utilizing dihydro-5-(2-propenyl)-2(3H)-furanone and L-lactide]

0.63 g (5.0 mmol) of dihydro-5-(2-propenyl)-2(3H)-furanone, 0.72 g (5.0 mmol) of L-lactide, 20 μ l of a 2M

toluene solution of diethyl zinc and 8 ml of a 0.01M
toluene solution of p-tert-butylbenzyl alcohol were
charged in a polymerization ampoule, then subjected to
a drying for 1 hour under a reduced pressure and a
5 nitrogen replacement, and the ampoule was sealed by
fusing under a reduced pressure and heated at 150°C to
execute a ring-opening polymerization. The reaction
was terminated after 10 hours and the mixture was
cooled. An obtained polymer was dissolved in
10 chloroform, and was re-precipitated in methanol of a 10
times amount of that of chloroform required for
dissolving. The precipitate was recovered and dried
under a reduced pressure to obtain 0.58 g of a polymer.
An NMR analysis conducted under conditions same as in
15 Example 6 for specifying the structure of the obtained
polymer confirmed as a polyhydroxyalkanoate constituted
of a unit represented by chemical formula (112) as the
monomer. It was also confirmed that a proportion of
the monomer units was unit A by 7 mol% and unit B by 93
20 mol%:

[0511]

[Chemical Formula 182]



[0512]

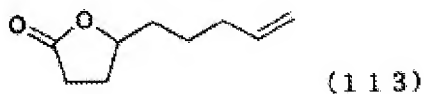
An average molecular weight of the obtained polyhydroxyalkanoate was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-GEL Super HM-H, solvent: chloroform, converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 7,200$ and a weight-averaged molecular weight $M_w = 9,300$.

10 [0513]

(Example 65)

[0514]

[Chemical Formula 183]



15 [0515]

[Polyester synthesis utilizing dihydro-5-(4-propenyl)-2(3H)-furanone represented by chemical formula (113) and δ -valerolactone]

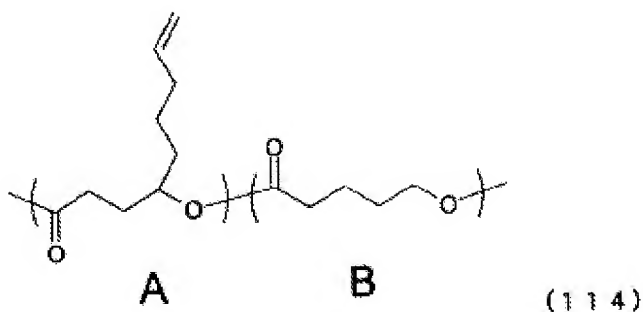
0.77 g (5.0 mmol) of dihydro-5-(4-propenyl)-2(3H)-furanone, 0.40 g (5.0 mmol) of δ -valerolactone, 20 μ l

20

of a 2M toluene solution of diethyl zinc and 8 ml of a
0.01M toluene solution of p-tert-butylbenzyl alcohol
were charged in a polymerization ampoule, then
subjected to a drying for 1 hour under a reduced
5 pressure and a nitrogen replacement, and the ampoule
was sealed by fusing under a reduced pressure and
heated at 150°C to execute a ring-opening
polymerization. The reaction was terminated after 10
hours and the mixture was cooled. An obtained polymer
10 was dissolved in chloroform, and was re-precipitated in
methanol of a 10 times amount of that of chloroform
required for dissolving. The precipitate was recovered
and dried under a reduced pressure to obtain 0.39 g of
a polymer. An NMR analysis conducted under conditions
15 same as in Example 6 for specifying the structure of
the obtained polymer confirmed as a
polyhydroxyalkanoate constituted of a unit represented
by chemical formula (114) as the monomer. It was also
confirmed that a proportion of the monomer units was
20 unit A by 5 mol% and unit B by 94 mol%:

[0516]

[Chemical Formula 184]



[0517]

An average molecular weight of the obtained polyhydroxyalkanoate was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-GEL Super HM-H, solvent: chloroform, converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 6,400$ and a weight-averaged molecular weight $M_w = 8,600$.

10 [0518]

(Example 66)

[0519]

[Chemical Formula 185]



15 [0520]

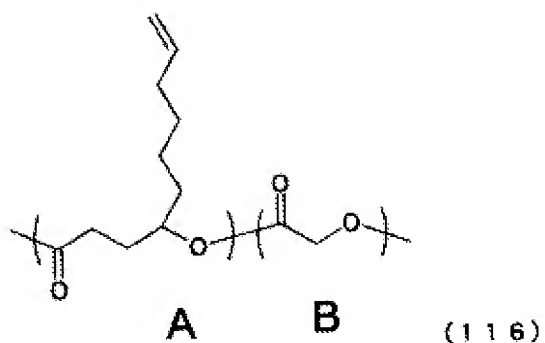
[Polyester synthesis utilizing dihydro-5-(5-hexenyl)-2(3H)-furanone and glycolide]

0.84 g (5.0 mmol) of dihydro-5-(5-hexenyl)-2(3H)-

furanone, 0.58 g (5.0 mmol) of glycolide, 20 µl of a 2M
toluene solution of diethyl zinc and 8 ml of a 0.01M
toluene solution of p-tert-butylbenzyl alcohol were
charged in a polymerization ampoule, then subjected to
5 a drying for 1 hour under a reduced pressure and a
nitrogen replacement, and the ampoule was sealed by
fusing under a reduced pressure and heated at 150°C to
execute a ring-opening polymerization. The reaction
was terminated after 10 hours and the mixture was
10 cooled. An obtained polymer was dissolved in
chloroform, and was re-precipitated in methanol of a 10
times amount of that of chloroform required for
dissolving. The precipitate was recovered and dried
under a reduced pressure to obtain 0.53 g of a polymer.
15 An NMR analysis conducted under conditions same as in
Example 6 for specifying the structure of the obtained
polymer confirmed as a polyhydroxyalkanoate constituted
of a unit represented by chemical formula (116) as the
monomer. It was also confirmed that a proportion of
20 the monomer units was unit A by 7 mol% and unit B by 93
mol%:

[0521]

[Chemical Formula 186]



[0522]

An average molecular weight of the obtained polyhydroxyalkanoate was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-GEL Super HM-H, solvent: chloroform, converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 6,800$ and a weight-averaged molecular weight $M_w = 8,800$.

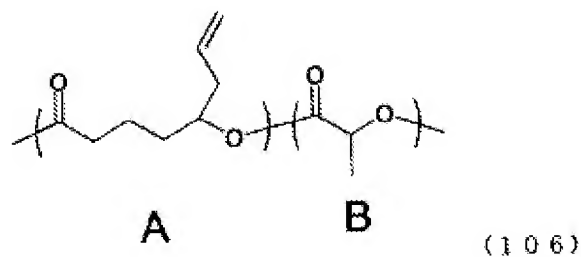
10 [0523]

(Example 67)

Oxidation reaction of a polyhydroxyalkanoate constituted of a unit represented by chemical formula (106) synthesized in Example 60

15 [0524]

[Chemical Formula 187]



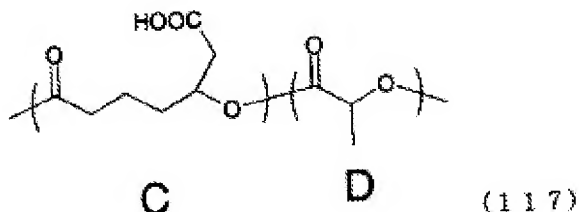
[0525]

0.50 g of polyhydroxyalkanoate (A: 11 mol%, B: 89 mol%) obtained in Example 60 and constituted of a unit
5 represented by chemical formula (106) were placed in an eggplant-shaped flask, and dissolved by adding 30 ml of acetone. The solution was placed in an ice bath and agitated while added 5 ml of acetic acid and 0.55 g of 18-crown-6-ether. Then 0.44 g of potassium
10 permanganate was slowly added in the ice bath and the mixture was agitated for 2 hours in the ice bath and further 18 hours at the room temperature. After the reaction, 60 ml of ethyl acetate and further 45 ml of water were added. Next, sodium hydrogen sulfite was
15 added until overacidity was removed. Then, the liquid factor was made to pH = 1 by 1.0 N of hydrochloric acid. The organic layer was separated. The organic layer was recovered and washed three times with 1.0 N of hydrochloric acid. After recovering the organic
20 layer, the solvent was distilled off to recover a crude polymer. Next, the polymer was recovered after cleaning with 50 ml of water and 50 ml of methanol, and

then cleaning three times with 50 ml of water. It was then dissolved in THF, and was re-precipitated in methanol of a 50-times amount of that of THF required for dissolving. The precipitate was recovered and
5 dried under a reduced pressure to obtain 0.43 g of polymer. An NMR analysis conducted under conditions same as in Example 6 for specifying the structure of the obtained polymer confirmed a polyhydroxyalkanoate containing units represented by chemical formula (117)
10 as monomer units.

[0526]

[Chemical Formula 188]



[0527]

15 An average molecular weight of the obtained polyhydroxyalkanoate was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-GEL Super HM-H, solvent: chloroform, converted as polystyrene). As a result, there were obtained a
20 number-averaged molecular weight $M_n = 98,500$ and a weight-averaged molecular weight $M_w = 166,400$.

Furthermore, in order to calculate the units of the obtained polyhydroxyalkanoate, the calculation was

made by methyl esterification of the carboxyl group at the end of the side chain of the polyhydroxyalkanoate using trimethylsilyl diazomethane. 30 mg of the targeted polyhydroxyalkanoate were placed in a 100-ml eggplant-shaped flask and dissolved by adding 2.1 ml of chloroform and 0.7 ml of methanol. Then 0.5 ml of a 2 mol/L hexane solution of trimethylsilyl diazomethane were added and the mixture was agitated for 1 hour at the room temperature. After the reaction, the solvent was distilled off to recover the polymer. The polymer was washed with 50 ml of methanol, then recovered, and dried under a reduced pressure to obtain 29 mg of polyhydroxyalkanoate. An NMR analysis conducted under conditions same as in Example 6 confirmed that a proportion of the units of the polyhydroxyalkanoate represented by chemical formula (117) was a copolymer as unit C by 10 mol% and unit D by 90 mol%.

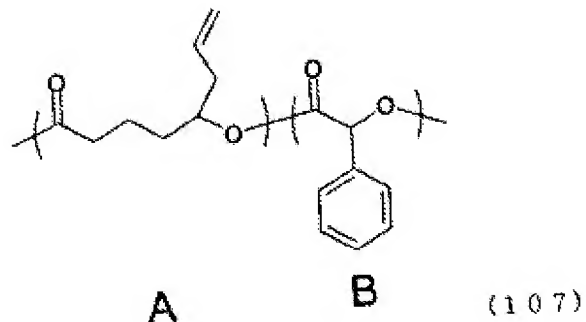
[0528]

(Example 68)

Oxidation reaction of a polyhydroxyalkanoate constituted of a unit represented by chemical formula (107) synthesized in Example 61

[0529]

[Chemical Formula 189]



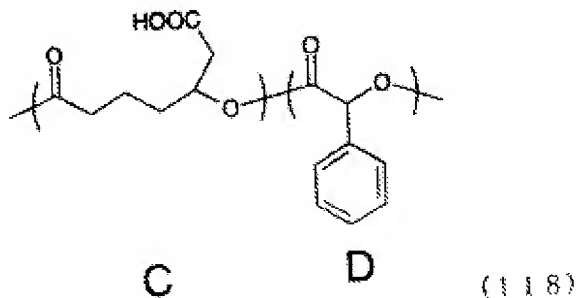
[0530]

0.50 g of polyhydroxyalkanoate (A: 12 mol%, B: 88 mol%) obtained in Example 61 and constituted of a unit represented by chemical formula (107) were placed in an eggplant-shaped flask, and dissolved by adding 30 ml of acetone. The solution was placed in an ice bath and agitated while added 5 ml of acetic acid and 0.35 g of 18-crown-6-ether. Then 0.28 g of potassium permanganate was slowly added in the ice bath and the mixture was agitated for 2 hours in the ice bath and further 18 hours at the room temperature. After the reaction, 60 ml of ethyl acetate and further 45 ml of water were added. Next, sodium hydrogen sulfite was added until overacidity was removed. Then, the liquid factor was made to pH = 1 by 1.0 N of hydrochloric acid. The organic layer was separated. The organic layer was recovered and washed three times with 1.0 N of hydrochloric acid. After recovering the organic layer, the solvent was distilled off to recover a crude polymer. Next, the polymer was recovered after

cleaning with 50 ml of water and 50 ml of methanol, and then cleaning three times with 50 ml of water. It was then dissolved in THF, and was re-precipitated in methanol of a 50-times amount of that of THF required
5 for dissolving. The precipitate was recovered and dried under a reduced pressure to obtain 0.44 g of polymer. An NMR analysis conducted under conditions same as in Example 6 for specifying the structure of the obtained polymer confirmed a polyhydroxyalkanoate
10 containing units represented by chemical formula (118) as monomer units.

[0531]

[Chemical Formula 190]



15 [0532]

An average molecular weight of the obtained polyhydroxyalkanoate was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-GEL Super HM-H, solvent: chloroform, converted as
20 polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 8,400$ and a

weight-averaged molecular weight $M_w = 16,300$.

Furthermore, in order to calculate the units of the obtained polyhydroxyalkanoate, the calculation was made by methyl esterification of the carboxyl group at the end of the side chain of the polyhydroxyalkanoate using trimethylsilyl diazomethane. 30 mg of the targeted polyhydroxyalkanoate were placed in a 100-ml eggplant-shaped flask and dissolved by adding 2.1 ml of chloroform and 0.7 ml of methanol. Then 0.5 ml of a 2 mol/L hexane solution of trimethylsilyl diazomethane were added and the mixture was agitated for 1 hour at the room temperature. After the reaction, the solvent was distilled off to recover the polymer. The polymer was washed with 50 ml of methanol, then recovered, and dried under a reduced pressure to obtain 30 mg of polyhydroxyalkanoate.

[0533]

An NMR analysis conducted under conditions same as in Example 6 confirmed that a proportion of the units of the polyhydroxyalkanoate represented by chemical formula (118) was a copolymer as unit C by 11 mol% and unit D by 89 mol%.

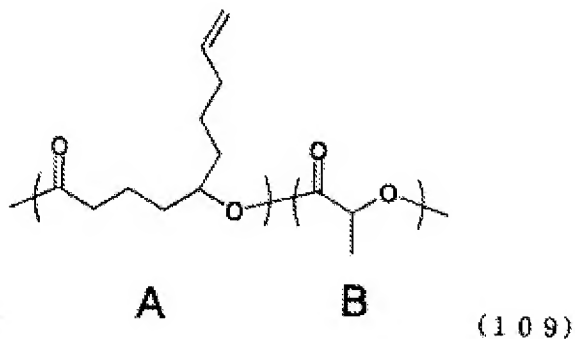
[0534]

(Example 69)

Oxidation reaction of a polyhydroxyalkanoate constituted of a unit represented by chemical formula (109) synthesized in Example 62

[0535]

[Chemical Formula 191]



[0536]

5 0.50 g of polyhydroxyalkanoate (A: 8 mol%, B: 92 mol%) obtained in Example 62 and constituted of a unit represented by chemical formula (109) were placed in an eggplant-shaped flask, and dissolved by adding 30 ml of acetone. The solution was placed in an ice bath and

10 agitated while added 5 ml of acetic acid and 0.40 g of 18-crown-6-ether. Then 0.32 g of potassium permanganate was slowly added in the ice bath and the mixture was agitated for 2 hours in the ice bath and further 18 hours at the room temperature. After the

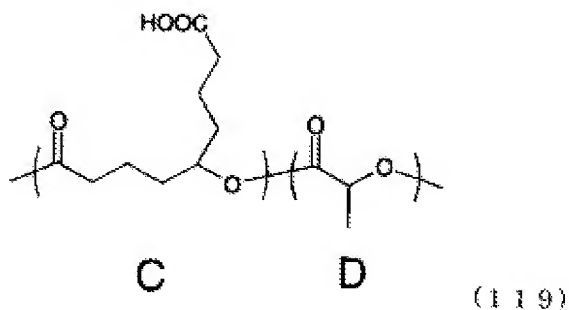
15 reaction, 60 ml of ethyl acetate and further 45 ml of water were added. Next, sodium hydrogen sulfite was added until overacidity was removed. Then, the liquid factor was made to pH = 1 by 1.0 N of hydrochloric acid. The organic layer was separated. The organic

20 layer was recovered and washed three times with 1.0 N of hydrochloric acid. After recovering the organic

layer, the solvent was distilled off to recover a crude polymer. Next, the polymer was recovered after cleaning with 50 ml of water and 50 ml of methanol, and then cleaning three times with 50 ml of water. It was
5 then dissolved in THF, and was re-precipitated in methanol of a 50-times amount of that of THF required for dissolving. The precipitate was recovered and dried under a reduced pressure to obtain 0.43 g of polymer. An NMR analysis conducted under conditions
10 same as in Example 6 for specifying the structure of the obtained polymer confirmed a polyhydroxyalkanoate containing units represented by chemical formula (119) as monomer units.

[0537]

15 [Chemical Formula 192]



[0538]

An average molecular weight of the obtained polyhydroxyalkanoate was evaluated by gel permeation
20 chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-GEL Super HM-H, solvent: chloroform, converted as polystyrene). As a result, there were obtained a

number-averaged molecular weight $M_n = 32,500$ and a weight-averaged molecular weight $M_w = 59,500$.

Furthermore, in order to calculate the units of the obtained polyhydroxyalkanoate, the calculation was made by methyl esterification of the carboxyl group at the end of the side chain of the polyhydroxyalkanoate using trimethylsilyl diazomethane. 30 mg of the targeted polyhydroxyalkanoate were placed in a 100-ml eggplant-shaped flask and dissolved by adding 2.1 ml of chloroform and 0.7 ml of methanol. Then 0.5 ml of a 2 mol/L hexane solution of trimethylsilyl diazomethane were added and the mixture was agitated for 1 hour at the room temperature. After the reaction, the solvent was distilled off to recover the polymer. The polymer was washed with 50 ml of methanol, then recovered, and dried under a reduced pressure to obtain 28 mg of polyhydroxyalkanoate.

[0539]

An NMR analysis conducted under conditions same as in Example 6 confirmed that a proportion of the units of the polyhydroxyalkanoate represented by chemical formula (119) was a copolymer as unit C by 7 mol% and unit D by 93 mol%.

[0540]

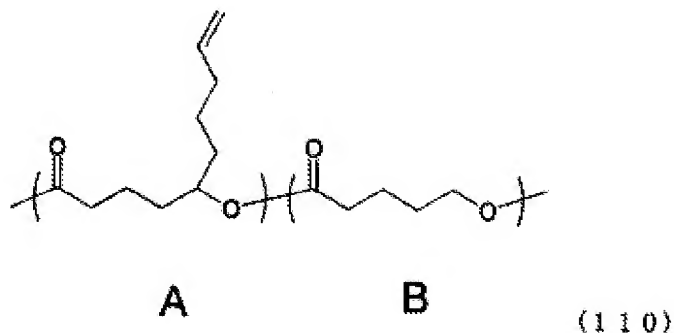
(Example 70)

Oxidation reaction of a polyhydroxyalkanoate constituted of a unit represented by chemical formula

(110) synthesized in Example 63

[0541]

[Chemical Formula 193]



5 [0542]

0.50 g of polyhydroxyalkanoate (A: 8 mol%, B: 92 mol%) obtained in Example 63 and constituted of a unit represented by chemical formula (110) were placed in an eggplant-shaped flask, and dissolved by adding 30 ml of acetone. The solution was placed in an ice bath and agitated while added 5 ml of acetic acid and 0.30 g of 18-crown-6-ether. Then 0.24 g of potassium permanganate was slowly added in the ice bath and the mixture was agitated for 2 hours in the ice bath and further 18 hours at the room temperature. After the reaction, 60 ml of ethyl acetate and further 45 ml of water were added. Next, sodium hydrogen sulfite was added until overacidity was removed. Then, the liquid factor was made to pH = 1 by 1.0 N of hydrochloric acid. The organic layer was separated. The organic layer was recovered and washed three times with 1.0 N

10

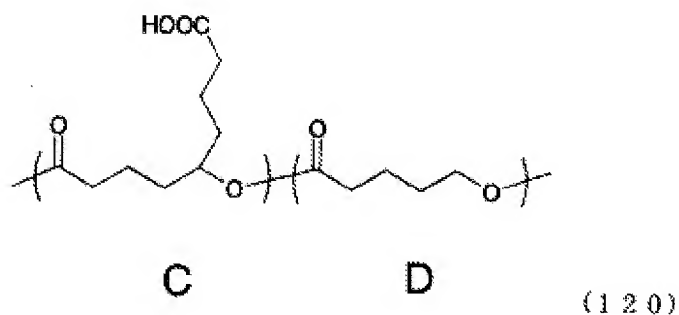
15

20

of hydrochloric acid. After recovering the organic layer, the solvent was distilled off to recover a crude polymer. Next, the polymer was recovered after cleaning with 50 ml of water and 50 ml of methanol, and then cleaning three times with 50 ml of water. It was then dissolved in THF, and was re-precipitated in methanol of a 50-times amount of that of THF required for dissolving. The precipitate was recovered and dried under a reduced pressure to obtain 0.42 g of polymer. An NMR analysis conducted under conditions same as in Example 6 for specifying the structure of the obtained polymer confirmed a polyhydroxyalkanoate containing units represented by chemical formula (120) as monomer units.

[0543]

[Chemical Formula 194]



[0544]

An average molecular weight of the obtained polyhydroxyalkanoate was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-

GEL Super HM-H, solvent: chloroform, converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 7,300$ and a weight-averaged molecular weight $M_w = 9,900$.

5 Furthermore, in order to calculate the units of the obtained polyhydroxyalkanoate, the calculation was made by methyl esterification of the carboxyl group at the end of the side chain of the polyhydroxyalkanoate using trimethylsilyl diazomethane. 30 mg of the
10 targeted polyhydroxyalkanoate were placed in a 100-ml eggplant-shaped flask and dissolved by adding 2.1 ml of chloroform and 0.7 ml of methanol. Then 0.5 ml of a 2 mol/L hexane solution of trimethylsilyl diazomethane were added and the mixture was agitated for 1 hour at
15 the room temperature. After the reaction, the solvent was distilled off to recover the polymer. The polymer was washed with 50 ml of methanol, then recovered, and dried under a reduced pressure to obtain 27 mg of polyhydroxyalkanoate.

20 [0545]

 An NMR analysis conducted under conditions same as in Example 6 confirmed that a proportion of the units of the polyhydroxyalkanoate represented by chemical formula (120) was a copolymer as unit C by 7 mol% and
25 unit D by 93 mol%.

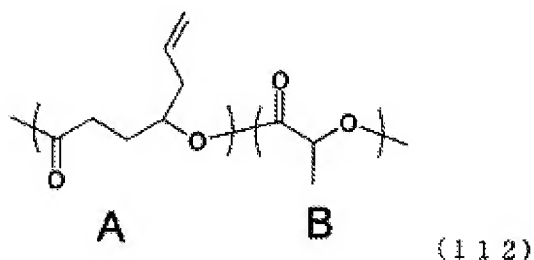
[0546]

(Example 71)

Oxidation reaction of a polyhydroxyalkanoate constituted of a unit represented by chemical formula (112) synthesized in Example 64

[0547]

5 [Chemical Formula 195]



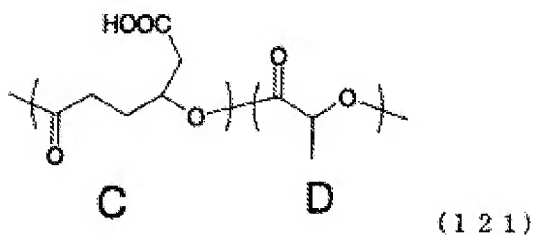
[0548]

0.50 g of polyhydroxyalkanoate (A: 7 mol%, B: 93 mol%) obtained in Example 64 and constituted of a unit represented by chemical formula (112) were placed in an
10 eggplant-shaped flask, and dissolved by adding 30 ml of acetone. The solution was placed in an ice bath and agitated while added 5 ml of acetic acid and 0.37 g of 18-crown-6-ether. Then 0.29 g of potassium
15 permanganate was slowly added in the ice bath and the mixture was agitated for 2 hours in the ice bath and further 18 hours at the room temperature. After the reaction, 60 ml of ethyl acetate and further 45 ml of water were added. Next, sodium hydrogen sulfite was
20 added until overacidity was removed. Then, the liquid factor was made to pH = 1 by 1.0 N of hydrochloric acid. The organic layer was separated. The organic

layer was recovered and washed three times with 1.0 N
of hydrochloric acid. After recovering the organic
layer, the solvent was distilled off to recover a crude
polymer. Next, the polymer was recovered after
5 cleaning with 50 ml of water and 50 ml of methanol, and
then cleaning three times with 50 ml of water. It was
then dissolved in THF, and was re-precipitated in
methanol of a 50-times amount of that of THF required
for dissolving. The precipitate was recovered and
10 dried under a reduced pressure to obtain 0.43 g of
polymer. An NMR analysis conducted under conditions
same as in Example 6 for specifying the structure of
the obtained polymer confirmed a polyhydroxyalkanoate
containing units represented by chemical formula (121)
15 as monomer units.

[0549]

[Chemical Formula 196]



[0550]

20 An average molecular weight of the obtained
polyhydroxyalkanoate was evaluated by gel permeation
chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-
GEL Super HM-H, solvent: chloroform, converted as

polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 6,400$ and a weight-averaged molecular weight $M_w = 8,400$.

Furthermore, in order to calculate the units of
5 the obtained polyhydroxyalkanoate, the calculation was made by methyl esterification of the carboxyl group at the end of the side chain of the polyhydroxyalkanoate using trimethylsilyl diazomethane. 30 mg of the targeted polyhydroxyalkanoate were placed in a 100-ml
10 eggplant-shaped flask and dissolved by adding 2.1 ml of chloroform and 0.7 ml of methanol. Then 0.5 ml of a 2 mol/L hexane solution of trimethylsilyl diazomethane were added and the mixture was agitated for 1 hour at the room temperature. After the reaction, the solvent
15 was distilled off to recover the polymer. The polymer was washed with 50 ml of methanol, then recovered, and dried under a reduced pressure to obtain 27 mg of polyhydroxyalkanoate.

[0551]

20 An NMR analysis conducted under conditions same as in Example 6 confirmed that a proportion of the units of the polyhydroxyalkanoate represented by chemical formula (121) was a copolymer as unit C by 7 mol% and unit D by 93 mol%.

25 [0552]

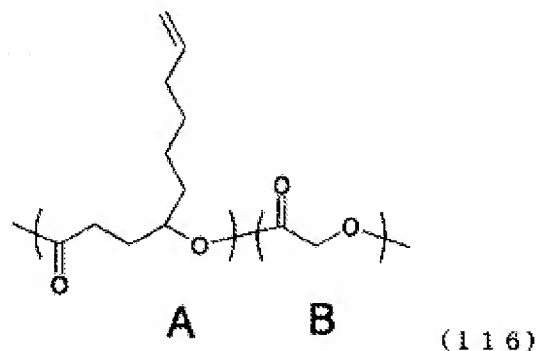
(Example 72)

Oxidation reaction of a polyhydroxyalkanoate

constituted of a unit represented by chemical formula
(116) synthesized in Example 66

[0553]

[Chemical Formula 197]



5

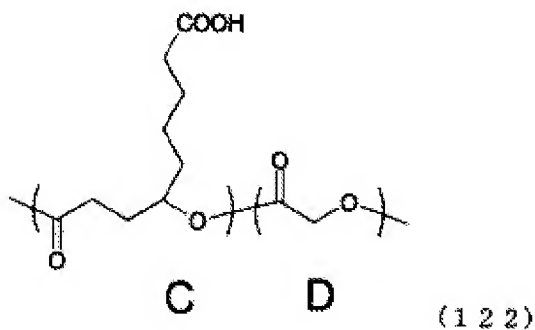
[0554]

0.50 g of polyhydroxyalkanoate (A: 7 mol%, B: 93 mol%) obtained in Example 66 and constituted of a unit represented by chemical formula (116) were placed in an
10 eggplant-shaped flask, and dissolved by adding 30 ml of acetone. The solution was placed in an ice bath and agitated while added 5 ml of acetic acid and 0.42 g of 18-crown-6-ether. Then 0.34 g of potassium
permanganate was slowly added in the ice bath and the
15 mixture was agitated for 2 hours in the ice bath and further 18 hours at the room temperature. After the reaction, 60 ml of ethyl acetate and further 45 ml of water were added. Next, sodium hydrogen sulfite was added until overacidity was removed. Then, the liquid
20 factor was made to pH = 1 by 1.0 N of hydrochloric acid. The organic layer was separated. The organic

layer was recovered and washed three times with 1.0 N
of hydrochloric acid. After recovering the organic
layer, the solvent was distilled off to recover a crude
polymer. Next, the polymer was recovered after
5 cleaning with 50 ml of water and 50 ml of methanol, and
then cleaning three times with 50 ml of water. It was
then dissolved in THF, and was re-precipitated in
methanol of a 50-times amount of that of THF required
for dissolving. The precipitate was recovered and
10 dried under a reduced pressure to obtain 0.45 g of
polymer. An NMR analysis conducted under conditions
same as in Example 6 for specifying the structure of
the obtained polymer confirmed a polyhydroxyalkanoate
containing units represented by chemical formula (122)
15 as monomer units.

[0555]

[Chemical Formula 198]



[0556]

20 An average molecular weight of the obtained
polyhydroxyalkanoate was evaluated by gel permeation

chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-GEL Super HM-H, solvent: chloroform, converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 6,200$ and a
5 weight-averaged molecular weight $M_w = 8,400$.
[0557]

Furthermore, in order to calculate the units of the obtained polyhydroxyalkanoate, the calculation was made by methyl esterification of the carboxyl group at
10 the end of the side chain of the polyhydroxyalkanoate using trimethylsilyl diazomethane. 30 mg of the targeted polyhydroxyalkanoate were placed in a 100-ml eggplant-shaped flask and dissolved by adding 2.1 ml of chloroform and 0.7 ml of methanol. Then 0.5 ml of a 2
15 mol/L hexane solution of trimethylsilyl diazomethane were added and the mixture was agitated for 1 hour at the room temperature. After the reaction, the solvent was distilled off to recover the polymer. The polymer was washed with 50 ml of methanol, then recovered, and
20 dried under a reduced pressure to obtain 28 mg of polyhydroxyalkanoate.
[0558]

An NMR analysis conducted under conditions same as in Example 6 confirmed that a proportion of the units
25 of the polyhydroxyalkanoate represented by chemical formula (122) was a copolymer as unit C by 7 mol% and unit D by 93 mol%.

[0559]

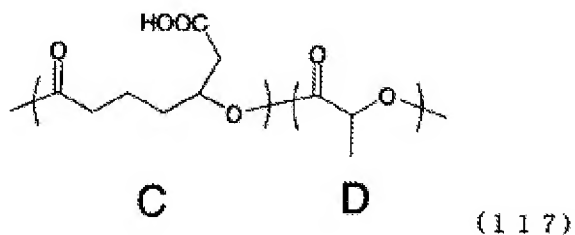
(Example 73)

Condensation reaction of a polyhydroxyalkanoate constituted of a unit represented by chemical formula

5 (117) synthesized in Example 67 with 2-aminobenzenesulfonic acid

[0560]

[Chemical Formula 199]



10 [0561]

In a nitrogen atmosphere, 0.40 g of polymer synthesized with polyhydroxyalkanoate copolymer (C: 10 mol%, D: 90 mol%) obtained in Example 67 and constituted of a unit represented by chemical formula

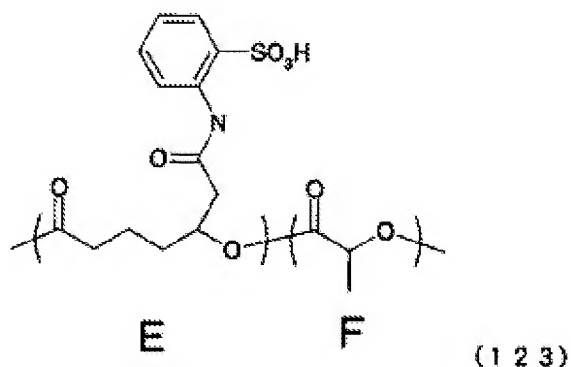
15 (117) and 0.43 g of 2-aminobenzenesulfonic acid were placed in a 100-ml three-necked flask, agitated with 15.0 ml of pyridine, further added with 1.29 ml of triphenyl phosphite and heated for 6 hours at 120°C. After the reaction, the polymer was recovered by a re-
20 precipitation in 150 ml of ethanol. The obtained polymer was washed with 1N hydrochloric acid for 1 day, then washed by an agitation in water for 1 day and dried under a reduced pressure to obtain 0.34 g of a

polymer. The structure of the obtained polymer was analyzed by ^1H -NMR (FT-NMR: Bruker DPX 400, resonance frequency: 400 MHz, measured species: ^1H , solvent: deuterized DMSO, temperature: room temperature) and a
5 Fourier transformed infrared absorption (FT-IR) spectrum (Nicolet AVATAR 360FT-IR). The IR measurement showed a decrease of a peak at 1695 cm^{-1} attributable to a carboxylic acid, and a new peak at 1658 cm^{-1} attributable to an amide group.

10 A result of ^1H -NMR confirmed, by a shift in a peak resulting from an aromatic ring of the 2-aminobenzenesulfonic acid structure, that the polymer was a polyhydroxyalkanoate containing units represented by chemical formula (123) as monomer units.

15 [0562]

[Chemical Formula 200]



[0563]

It was also confirmed that a proportion of the
20 units of the polyhydroxyalkanoate represented by chemical formula (123) was a copolymer as unit E by 10

mol% and unit F by 90 mol%. An average molecular weight of the obtained polymer was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8120, column: Polymer Laboratories PLgel 5 μ MIXED-C, solvent:

5 DMF/LiBr 0.1 %(w/v), converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 83,500$ and a weight-averaged molecular weight $M_w = 146,500$.

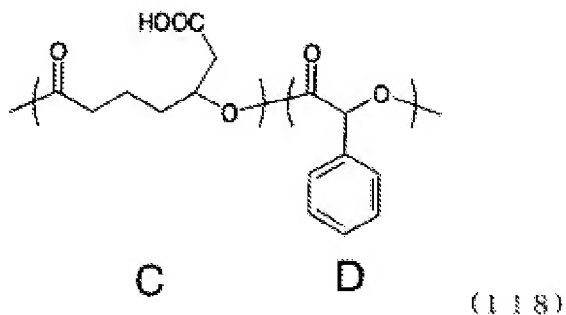
[0564]

10 (Example 74)

Condensation reaction of a polyhydroxyalkanoate constituted of a unit represented by chemical formula (118) synthesized in Example 68 with 4-methoxyaniline-2-sulfonic acid

15 [0565]

[Chemical Formula 201]



[0566]

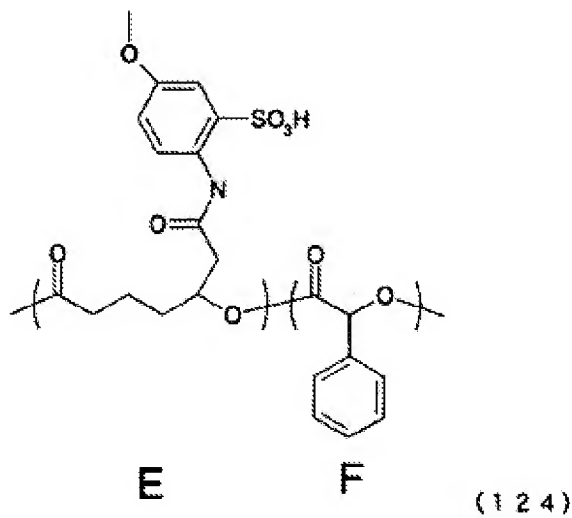
In a nitrogen atmosphere, 0.40 g of polymer
20 synthesized with polyhydroxyalkanoate copolymer (C: 11 mol%, D: 89 mol%) obtained in Example 68 and

constituted of a unit represented by chemical formula (118) and 0.33 g of 4-methoxyaniline-2-sulfonic acid were placed in a 100-ml three-necked flask, agitated with 15.0 ml of pyridine, further added with 0.84 ml of triphenyl phosphite and heated for 6 hours at 120°C. After the reaction, the polymer was recovered by a re-precipitation in 150 ml of ethanol. The obtained polymer was washed with 1N hydrochloric acid for 1 day, then washed by an agitation in water for 1 day and dried under a reduced pressure to obtain 0.35 g of a polymer. The structure of the obtained polymer was analyzed by ^1H -NMR (FT-NMR: Bruker DPX 400, resonance frequency: 400 MHz, measured species: ^1H , solvent: deuterized DMSO, temperature: room temperature) and a Fourier transformed infrared absorption (FT-IR) spectrum (Nicolet AVATAR 360FT-IR). The IR measurement showed a decrease of a peak at 1695 cm^{-1} attributable to a carboxylic acid, and a new peak at 1658 cm^{-1} attributable to an amide group.

A result of ^1H -NMR confirmed, by a shift in a peak resulting from an aromatic ring of the 4-methoxyaniline-2-sulfonic acid structure, that the polymer was a polyhydroxyalkanoate containing units represented by chemical formula (124) as monomer units.

[0567]

[Chemical Formula 202]



[0568]

It was also confirmed that a proportion of the units of the polyhydroxyalkanoate represented by chemical formula (124) was a copolymer as unit E by 11 mol% and unit F by 89 mol%. An average molecular weight of the obtained polymer was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8120, column: Polymer Laboratories PLgel 5 μ MIXED-C, solvent: DMF/LiBr 0.1 % (w/v), converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 8,400$ and a weight-averaged molecular weight $M_w = 16,400$.

[0569]

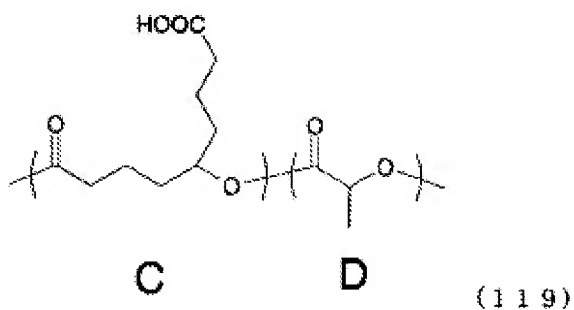
15 (Example 75)

Condensation reaction of a polyhydroxyalkanoate constituted of a unit represented by chemical formula (119) synthesized in Example 69 with 2-amino-1-

naphthalenesulfonic acid

[0570]

[Chemical Formula 203]



5 [0571]

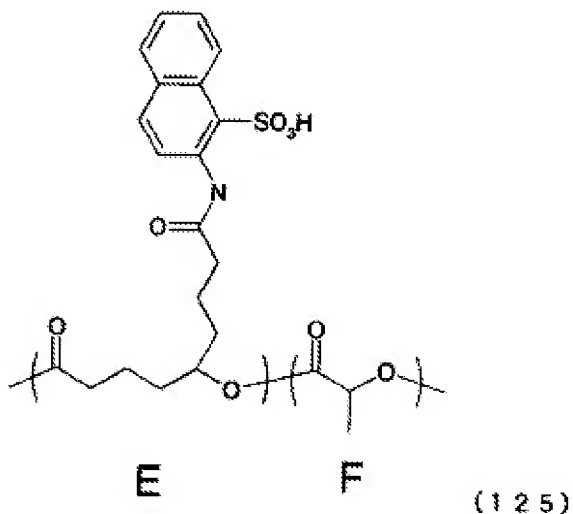
In a nitrogen atmosphere, 0.40 g of polymer synthesized with polyhydroxyalkanoate copolymer (C: 7 mol%, D: 93 mol%) obtained in Example 69 and constituted of a unit represented by chemical formula
10 (119) and 0.39 g of 2-amino-1-naphthalenesulfonic acid were placed in a 100-ml three-necked flask, agitated with 15.0 ml of pyridine, further added with 0.91 ml of triphenyl phosphite and heated for 6 hours at 120°C. After the reaction, the polymer was recovered by a re-
15 precipitation in 150 ml of ethanol. The obtained polymer was washed with 1N hydrochloric acid for 1 day, then washed by an agitation in water for 1 day and dried under a reduced pressure to obtain 0.34 g of a polymer. The structure of the obtained polymer was
20 analyzed by ¹H-NMR (FT-NMR: Bruker DPX 400, resonance frequency: 400 MHz, measured species: ¹H, solvent:

deuterized DMSO, temperature: room temperature) and a Fourier transformed infrared absorption (FT-IR) spectrum (Nicolet AVATAR 360FT-IR). The IR measurement showed a decrease of a peak at 1695 cm^{-1} attributable to a carboxylic acid, and a new peak at 1658 cm^{-1} attributable to an amide group.

A result of ^1H -NMR confirmed, by a shift in a peak resulting from an aromatic ring of the 2-amino-1-naphthalenesulfonic acid structure, that the polymer was a polyhydroxyalkanoate containing units represented by chemical formula (125) as monomer units.

[0572]

[Chemical Formula 204]



15 [0573]

It was also confirmed that a proportion of the units of the polyhydroxyalkanoate represented by chemical formula (125) was a copolymer as unit E by 7

mol% and unit F by 93 mol%. An average molecular weight of the obtained polymer was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8120, column: Polymer Laboratories PLgel 5 μ MIXED-C, solvent:

5 DMF/LiBr 0.1 %(w/v), converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 30,100$ and a weight-averaged molecular weight $M_w = 54,500$.

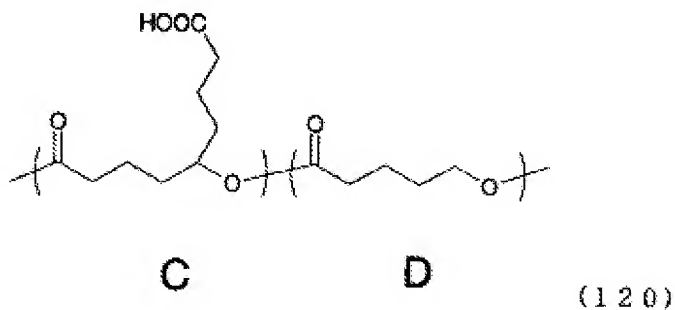
[0574]

10 (Example 76)

Condensation reaction of a polyhydroxyalkanoate constituted of a unit represented by chemical formula (120) synthesized in Example 70 with 2-amino-2-methyl propane sulfonic acid

15 [0575]

[Chemical Formula 205]



[0576]

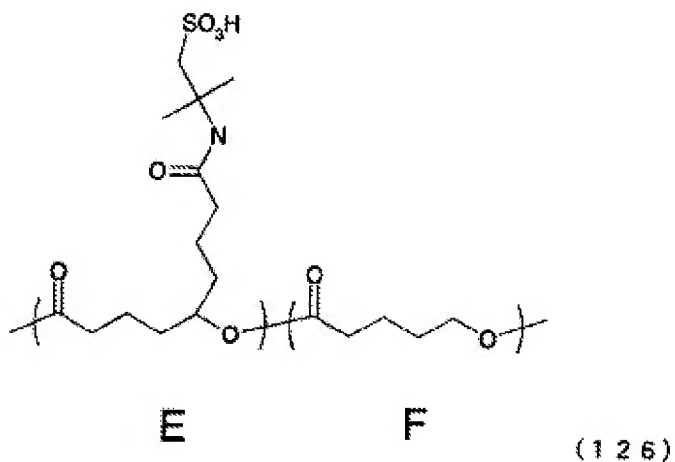
In a nitrogen atmosphere, 0.40 g of polymer
20 synthesized with polyhydroxyalkanoate copolymer (C: 7 mol%, D: 93 mol%) obtained in Example 70 and constituted of a unit represented by chemical formula

(120) and 0.20 g of 2-amino-2-methyl propane sulfonic acid were placed in a 100-ml three-necked flask, agitated with 15.0 ml of pyridine, further added with 0.69 ml of triphenyl phosphite and heated for 6 hours at 120°C. After the reaction, the polymer was recovered by a re-precipitation in 150 ml of ethanol. The obtained polymer was washed with 1N hydrochloric acid for 1 day, then washed by an agitation in water for 1 day and dried under a reduced pressure to obtain 0.32 g of a polymer. The structure of the obtained polymer was analyzed by ^1H -NMR (FT-NMR: Bruker DPX 400, resonance frequency: 400 MHz, measured species: ^1H , solvent: deuterized DMSO, temperature: room temperature) and a Fourier transformed infrared absorption (FT-IR) spectrum (Nicolet AVATAR 360FT-IR). The IR measurement showed a decrease of a peak at 1695 cm^{-1} attributable to a carboxylic acid, and a new peak at 1658 cm^{-1} attributable to an amide group.

A result of ^1H -NMR confirmed, by a shift in a peak resulting from a methylene of the 2-amino-2-methyl propane sulfonic acid structure, that the polymer was a polyhydroxyalkanoate containing units represented by chemical formula (126) as monomer units.

[0577]

[Chemical Formula 206]



[0578]

It was also confirmed that a proportion of the units of the polyhydroxyalkanoate represented by chemical formula (126) was a copolymer as unit E by 7 mol% and unit F by 93 mol%. An average molecular weight of the obtained polymer was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8120, column: Polymer Laboratories PLgel 5 μ MIXED-C, solvent: DMF/LiBr 0.1 % (w/v), converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 7,000$ and a weight-averaged molecular weight $M_w = 9,700$.

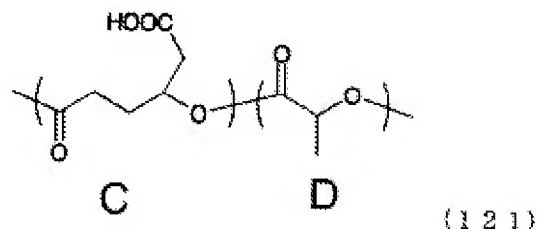
[0579]

15 (Example 77)

Condensation reaction of a polyhydroxyalkanoate constituted of a unit represented by chemical formula (121) synthesized in Example 71 with 2-aminobenzenesulfonic acid phenyl ester

[0580]

[Chemical Formula 207]



[0581]

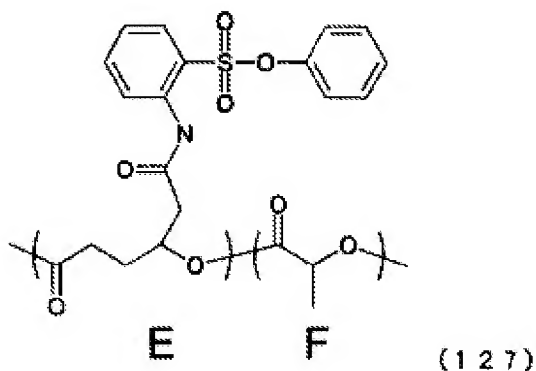
5 In a nitrogen atmosphere, 0.40 g of polymer
synthesized with polyhydroxyalkanoate copolymer (C: 7
mol%, D: 93 mol%) obtained in Example 71 and
constituted of a unit represented by chemical formula
(121) and 0.45 g of 2-aminobenzenesulfonic acid phenyl
10 ester were placed in a 100-ml three-necked flask,
agitated with 15.0 ml of pyridine, further added with
0.95 ml of triphenyl phosphite and heated for 6 hours
at 120°C. After the reaction, the polymer was
recovered by a re-precipitation in 150 ml of ethanol.
15 The obtained polymer was washed with 1N hydrochloric
acid for 1 day, then washed by an agitation in water
for 1 day and dried under a reduced pressure to obtain
0.36 g of a polymer. The structure of the obtained
polymer was analyzed by ¹H-NMR (FT-NMR: Bruker DPX 400,
20 resonance frequency: 400 MHz, measured species: ¹H,
solvent: deuterized DMSO, temperature: room
temperature) and a Fourier transformed infrared

absorption (FT-IR) spectrum (Nicolet AVATAR 360FT-IR). The IR measurement showed a decrease of a peak at 1695 cm^{-1} attributable to a carboxylic acid, and a new peak at 1658 cm^{-1} attributable to an amide group.

5 A result of ^1H -NMR confirmed, by a shift in a peak resulting from an aromatic ring of the 2-aminobenzenesulfonic acid phenyl ester structure, that the polymer was a polyhydroxyalkanoate containing units represented by chemical formula (127) as monomer units.

10 [0582]

[Chemical Formula 208]



[0583]

15 It was also confirmed that a proportion of the units of the polyhydroxyalkanoate represented by chemical formula (127) was a copolymer as unit E by 7 mol% and unit F by 93 mol%. An average molecular weight of the obtained polymer was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8120, column: Polymer Laboratories PLgel 5μ MIXED-C, solvent: 20 DMF/LiBr 0.1 %(w/v), converted as polystyrene). As a

result, there were obtained a number-averaged molecular weight $M_n = 6,200$ and a weight-averaged molecular weight $M_w = 8,200$.

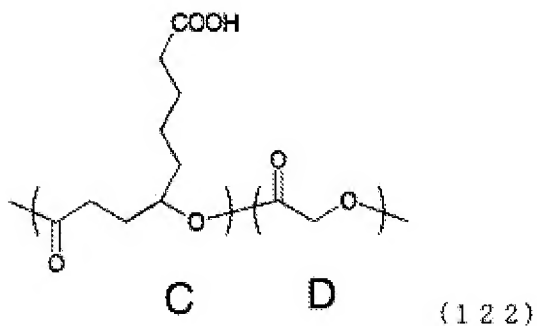
[0584]

5 (Example 78)

Condensation reaction of a polyhydroxyalkanoate constituted of a unit represented by chemical formula (122) synthesized in Example 72 with taurine

[0585]

10 [Chemical Formula 209]



[0586]

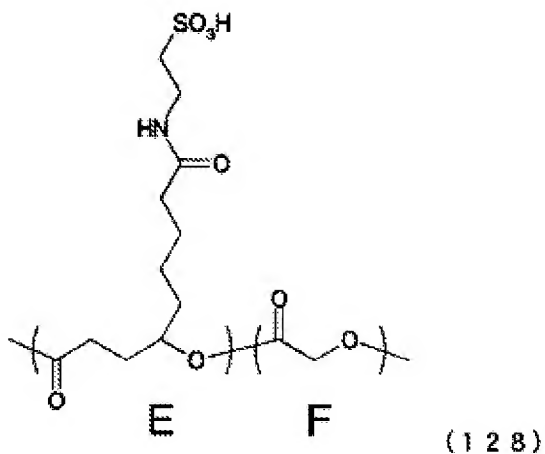
In a nitrogen atmosphere, 0.40 g of polymer synthesized with polyhydroxyalkanoate copolymer (C: 7
15 mol%, D: 93 mol%) obtained in Example 72 and constituted of a unit represented by chemical formula (122) and 0.26 g of taurine were placed in a 100-ml three-necked flask, agitated with 15.0 ml of pyridine, further added with 1.09 ml of triphenyl phosphite and
20 heated for 6 hours at 120°C. After the reaction, the

polymer was recovered by a re-precipitation in 150 ml
of ethanol. The obtained polymer was washed with 1N
hydrochloric acid for 1 day, then washed by an
agitation in water for 1 day and dried under a reduced
5 pressure to obtain 0.34 g of a polymer. The structure
of the obtained polymer was analyzed by ^1H -NMR (FT-NMR:
Bruker DPX 400, resonance frequency: 400 MHz, measured
species: ^1H , solvent: deuterized DMSO, temperature:
room temperature) and a Fourier transformed infrared
10 absorption (FT-IR) spectrum (Nicolet AVATAR 360FT-IR).
The IR measurement showed a decrease of a peak at 1695
 cm^{-1} attributable to a carboxylic acid, and a new peak
at 1658 cm^{-1} attributable to an amide group.

A result of ^1H -NMR confirmed, by a shift in a peak
15 resulting from a methylene of the taurine structure,
that the polymer was a polyhydroxyalkanoate containing
units represented by chemical formula (128) as monomer
units.

[0587]

20 [Chemical Formula 210]



[0588]

It was also confirmed that a proportion of the units of the polyhydroxyalkanoate represented by chemical formula (128) was a copolymer as unit E by 7 mol% and unit F by 93 mol%. An average molecular weight of the obtained polymer was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8120, column: Polymer Laboratories PLgel 5 μ MIXED-C, solvent: DMF/LiBr 0.1 % (w/v), converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 6,300$ and a weight-averaged molecular weight $M_w = 8,700$.

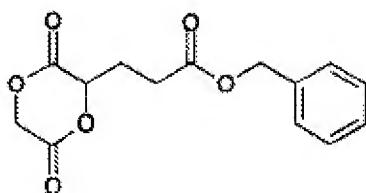
[0589]

(Example 79)

Synthesis of L-3-(2-benzyloxycarbonyl)ethyl-1,4-dioxane-2,5-dione represented by chemical formula (46)

[0590]

[Chemical Formula 211]



(46)

[0591]

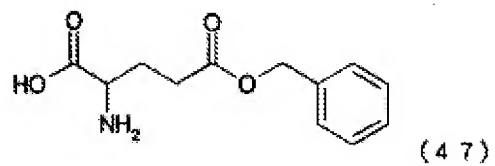
20 g of L-glutamine acid was dissolved in 200 ml of 80% sulfuric acid and reacted by adding 500 g of
5 benzyl alcohol while maintaining at 70°C. Then a crude product containing a compound represented by chemical formula (47) whose carboxyl group at the γ -position was protected was obtained. 100 g of this crude product was added to 1400 ml of 1N sulfuric acid, and while
10 agitating at 0 - 5°C, 100 ml of solution containing 45.2 g of sodium nitrite was dropped for about 3 hours, and the agitation was continued for 30 minutes. Furthermore, 30 ml of solution containing 9.4 g of sodium nitrite was dropped for about 30 minutes and the
15 mixture was left at the room temperature for one night. While being extracted by ether, the extracted solution was dried and concentrated using sodium sulfate and remaining coarse crystal was purified through a silica gel chromatography and recrystallization. Then a
20 compound represented by chemical formula (48) was obtained. 20 g of this compound and 17.4 g of bromoacetylchloride were dissolved in 300 ml of ether and cooled down to below 5°C, and 50 ml of ether

solution containing 9.5 g triethylamine (1.1 times in molar quantity) was dropped for 30 minutes. The reaction mixture was further agitated for 6 hours at the room temperature and filtrated. Then, 50 ml of water was added to the filtrated solution, which was agitated for 30 minutes. The solution was divided while adding water several times, and dried and concentrated after adding sodium sulfate to the ether layer. Then, 28.3 g of a compound represented by chemical formula (49) was obtained (yield: 94%).

DMF 50 ml solution of 10 g of the compound represented by chemical formula (49) was dropped to DMF 950 ml solution (heterogeneous solution) of 3.6 g of sodium hydrogencarbonate at the room temperature while taking about eight hours. Furthermore, the solution was reacted at the same temperature for 12 hours and filtrated, and the DMF was concentrated. The residue was cleaned by 50 ml of isopropanol. After the filtration, thus obtained white powder was dissolved in 200 ml of acetone, insoluble matters were removed, and the filtrate was concentrated. The residue was cleaned by a small amount of isopropanol, filtrated, and dried sufficiently. This white powder was sublimed and recrystallized by 400 ml of isopropanol. Then, 1.9 g (yield: 24%) of L-3-(2-benzyloxycarbonyl)ethyl-1,4-dioxane-2,5-dione represented by chemical formula (46) was obtained.

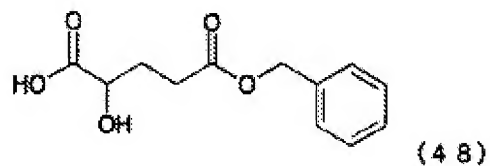
[0592]

[Chemical Formula 212]



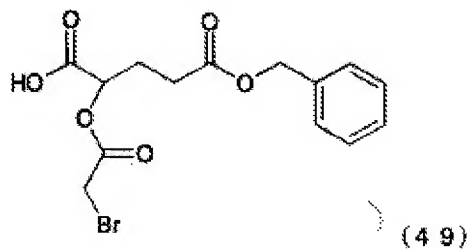
[0593]

5 [Chemical Formula 213]



[0594]

[Chemical Formula 214]



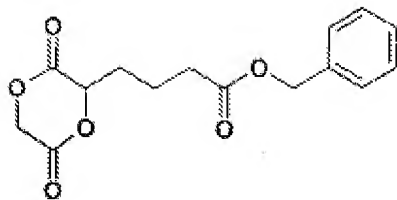
10 [0595]

(Example 80)

Synthesis of L-3-(3-benzyloxycarbonyl)propyl-1,4-dioxane-2,5-dione represented by chemical formula (129)

[0596]

15 [Chemical Formula 215]



(129)

[0597]

20 g of L-2-aminoadipic acid was dissolved in 200 ml of 80% sulfuric acid and reacted by adding 500 g of benzyl alcohol while maintaining at 70°C. Then a crude product containing a compound represented by chemical formula (130) whose carboxyl group at the 6-position was protected was obtained. 100 g of this crude product was added to 1400 ml of 1N sulfuric acid, and while agitating at 0 - 5°C, 100 ml of solution containing 41.7 g of sodium nitrite was dropped for about 3 hours, and the agitation was continued for 30 minutes. Furthermore, 30 ml of solution containing 8.9 g of sodium nitrite was dropped for about 30 minutes and the mixture was left at the room temperature for one night. While being extracted by ether, the extracted solution was dried and concentrated using sodium sulfate and remaining coarse crystal was purified through a silica gel chromatography and recrystallization. Then a compound represented by chemical formula (131) was obtained. 20 g of this compound and 16.4 g of bromoacetylchloride were dissolved in 300 ml of ether and cooled down to below

5°C, and 50 ml of ether solution containing 8.8 g triethylamine (1.1 times in molar quantity) was dropped for 30 minutes. The reaction mixture was further agitated for 6 hours at the room temperature and
5 filtrated. Then, 50 ml of water was added to the filtrated solution, which was agitated for 30 minutes. The solution was divided while adding water several times, and dried and concentrated after adding sodium sulfate to the ether layer. Then, 27.0 g of a compound
10 represented by chemical formula (132) was obtained (yield: 92%).

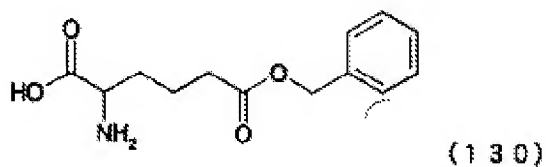
[0598]

DMF 50 ml solution of 10 g of the compound represented by chemical formula (132) was dropped to
15 DMF 950 ml solution (heterogeneous solution) of 3.4 g of sodium hydrogencarbonate at the room temperature while taking about eight hours. Furthermore, the solution was reacted at the same temperature for 12 hours and filtrated, and the DMF was concentrated. The
20 residue was cleaned by 50 ml of isopropanol. After the filtration, thus obtained white powder was dissolved in 200 ml of acetone, insoluble matters were removed, and the filtrate was concentrated. The residue was cleaned by a small amount of isopropanol, filtrated, and dried
25 sufficiently. This white powder was sublimed and recrystallized by 400 ml of isopropanol. Then, 2.1 g (yield: 26%) of L-3-(3-benzyloxycarbonyl)propyl-1,4-

dioxane-2,5-dione represented by chemical formula (129) was obtained.

[0599]

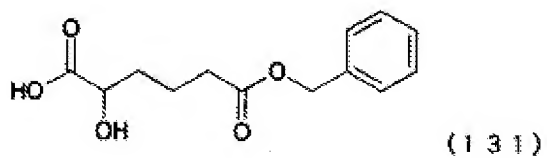
[Chemical Formula 216]



5

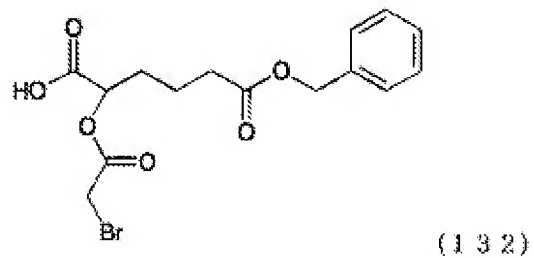
[0600]

[Chemical Formula 217]



[0601]

10 [Chemical Formula 218]



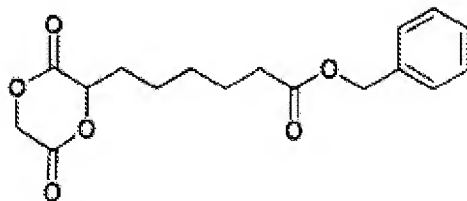
[0602]

(Example 81)

15 Synthesis of 3-(5-benzyloxycarbonyl)propyl-1,4-dioxane-2,5-dione represented by chemical formula (133)

[0603]

[Chemical Formula 219]



(133)

[0604]

20 g of 2-aminosebacic acid was dissolved in 200
5 ml of 80% sulfuric acid and reacted by adding 500 g of
benzyl alcohol while maintaining at 70°C. Then a crude
product containing a compound represented by chemical
formula (134) whose carboxyl group at the 8-position
was protected was obtained. 100 g of this crude
10 product was added to 1400 ml of 1N sulfuric acid, and
while agitating at 0 - 5°C, 100 ml of solution
containing 37.6 g of sodium nitrite was dropped for
about 3 hours, and the agitation was continued for 30
minutes. Furthermore, 30 ml of solution containing 8.0
15 g of sodium nitrite was dropped for about 30 minutes
and the mixture was left at the room temperature for
one night. While being extracted by ether, the
extracted solution was dried and concentrated using
sodium sulfate and remaining coarse crystal was
20 purified through a silica gel chromatography and
recrystallization. Then a compound represented by
chemical formula (135) was obtained. 20 g of this

compound and 14.7 g of bromoacetylchloride were dissolved in 300 ml of ether and cooled down to below 5°C, and 50 ml of ether solution containing 7.9 g triethylamine (1.1 times in molar quantity) was dropped
5 for 30 minutes. The reaction mixture was further agitated for 6 hours at the room temperature and filtrated. Then, 50 ml of water was added to the filtrated solution, which was agitated for 30 minutes. The solution was divided while adding water several
10 times, and dried and concentrated after adding sodium sulfate to the ether layer. Then, 25.8 g of a compound represented by chemical formula (136) was obtained (yield: 90%).

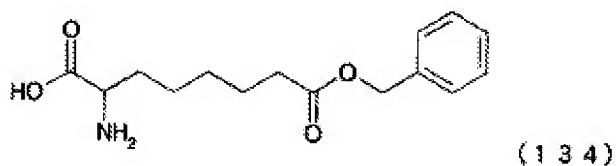
[0605]

15 DMF 50 ml solution of 10 g of the compound represented by chemical formula (136) was dropped to DMF 950 ml solution (heterogeneous solution) of 3.0 g of sodium hydrogencarbonate at the room temperature while taking about eight hours. Furthermore, the
20 solution was reacted at the same temperature for 12 hours and filtrated, and the DMF was concentrated. The residue was cleaned by 50 ml of isopropanol. After the filtration, thus obtained white powder was dissolved in 200 ml of acetone, insoluble matters were removed, and
25 the filtrate was concentrated. The residue was cleaned by a small amount of isopropanol, filtrated, and dried sufficiently. This white powder was sublimed and

recrystallized by 400 ml of isopropanol. Then, 2.0 g
(yield: 25%) of 3-(5-benzyloxycarbonyl)propyl-1,4-
dioxane-2,5-dione represented by chemical formula (133)
was obtained.

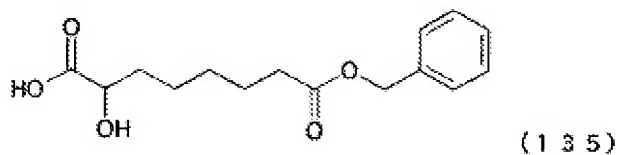
5 [0606]

[Chemical Formula 220]



[0607]

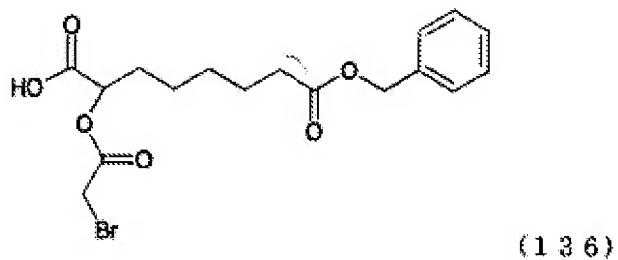
[Chemical Formula 221]



10

[0608]

[Chemical Formula 222]



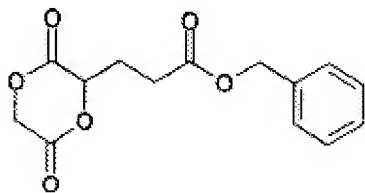
[0609]

15 (Example 82)

[Polyester synthesis utilizing L-3-(2-benzyloxycarbonyl)ethyl-1,4-dioxane-2,5-dione and L-lactide]

[0610]

5 [Chemical Formula 223]



(46)

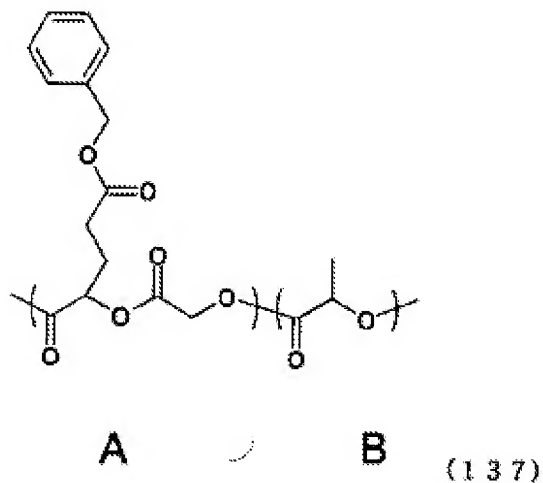
[0611]

0.29 g (1.0 mmol) of L-3-(2-benzyloxycarbonyl)ethyl-1,4-dioxane-2,5-dione
10 synthesized in Example 79, 1.44 g (10.0 mmol) of L-lactide and 4 ml of a 0.01M toluene solution of tin octylate (tin 2-ethylhexanoate) were charged in a polymerization ampoule, then subjected to a drying for 1 hour under a reduced pressure and a nitrogen
15 replacement, and the ampoule was sealed by fusing under a reduced pressure and heated at 150°C to execute a ring-opening polymerization. The reaction was terminated after 2 hours and the mixture was cooled. An obtained polymer was dissolved in chloroform, and
20 was re-precipitated in methanol of a 10 times amount of that of chloroform required for dissolving. The precipitate was recovered and dried under a reduced pressure to obtain 1.47 g of a polymer. An NMR

analysis conducted under conditions same as in Example
6 for specifying the structure of the obtained polymer
confirmed as a polyhydroxyalkanoate constituted of a
unit represented by chemical formula (137) as the
5 monomer. It was also confirmed that a proportion of
the monomer units was unit A by 6 mol% and unit B by 94
mol%:

[0612]

[Chemical Formula 224]



10

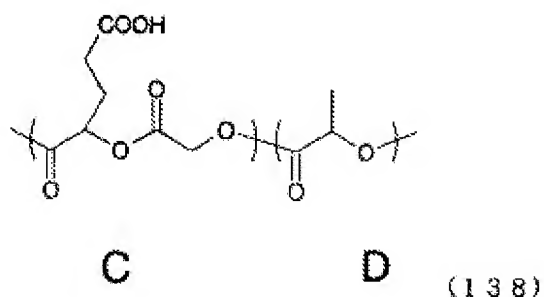
[0613]

An average molecular weight of the obtained
polyhydroxyalkanoate was evaluated by gel permeation
chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-
15 GEL Super HM-H, solvent: chloroform, converted as
polystyrene). As a result, there were obtained a
number-averaged molecular weight $M_n = 46,200$ and a
weight-averaged molecular weight $M_w = 61,900$. 1.00 g

of the obtained polyhydroxyalkanoate copolymer,
represented by the chemical formula (137), was
dissolved in 100 ml of a dioxane-ethanol mixed solvent
(75 : 25), then 0.22 g of a 5% palladium/carbon
5 catalyst were added, and the reaction system was
saturated with hydrogen and agitated for 1 day at the
room temperature. After the reaction, the catalyst was
removed by a filtration with a membrane filter of 0.25
µm, thereby recovering the reaction solution. The
10 solution was concentrated, then dissolved in
chloroform, and re-precipitated from methanol of a 10-
times amount. The obtained polymer was recovered and
dried under a reduced pressure to obtain 0.80 g of a
polymer. An NMR analysis conducted under conditions
15 same as in Example 6 for specifying the structure of
the obtained compound confirmed a polyhydroxyalkanoate
copolymer containing units represented by a chemical
formula (138) as monomer units. Also a proportion of
the monomer units was confirmed as unit C by 6 mol% and
20 unit D by 94 mol%.

[0614]

[Chemical Formula 225]



[0615]

An average molecular weight of the obtained polyhydroxyalkanoate was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-GEL Super HM-H, solvent: chloroform, converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 38,100$ and a weight-averaged molecular weight $M_w = 53,700$.

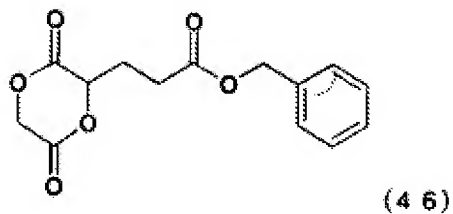
10 [0616]

(Example 83)

[Polyester synthesis utilizing L-3-(2-benzyloxycarbonyl)ethyl-1,4-dioxane-2,5-dione and L-lactide]

15 [0617]

[Chemical Formula 226]

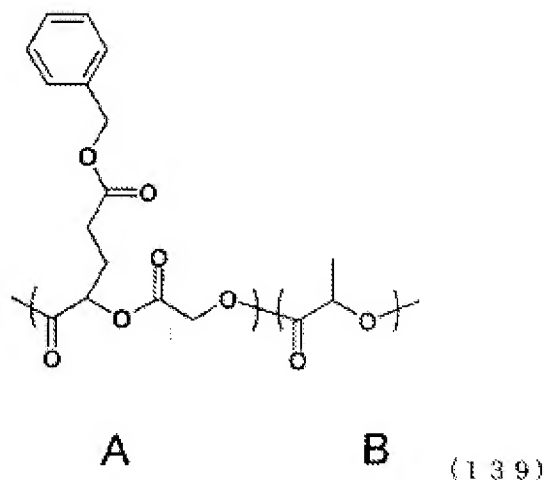


[0618]

0.56 g (2.0 mmol) of L-3-(2-benzyloxycarbonyl)ethyl-1,4-dioxane-2,5-dione synthesized in Example 79, 1.44 g (10.0 mmol) of L-lactide and 5 ml of a 0.01M toluene solution of tin octylate (tin 2-ethylhexanoate) were charged in a polymerization ampoule, then subjected to a drying for 1 hour under a reduced pressure and a nitrogen replacement, and the ampoule was sealed by fusing under a reduced pressure and heated at 150°C to execute a ring-opening polymerization. The reaction was terminated after 2 hours and the mixture was cooled. An obtained polymer was dissolved in chloroform, and was re-precipitated in methanol of a 10 times amount of that of chloroform required for dissolving. The precipitate was recovered and dried under a reduced pressure to obtain 1.70 g of a polymer. An NMR analysis conducted under conditions same as in Example 6 for specifying the structure of the obtained polymer confirmed as a polyhydroxyalkanoate constituted of a unit represented by chemical formula (139) as the monomer. It was also confirmed that a proportion of the monomer units was unit A by 12 mol% and unit B by 88 mol%:

[0619]

25 [Chemical Formula 227]



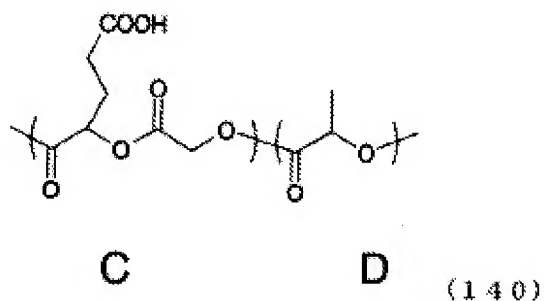
[0620]

An average molecular weight of the obtained polyhydroxyalkanoate was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-GEL Super HM-H, solvent: chloroform, converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 52,100$ and a weight-averaged molecular weight $M_w = 66,700$. 1.00 g of the obtained polyhydroxyalkanoate copolymer, represented by the chemical formula (139), was dissolved in 100 ml of a dioxane-ethanol mixed solvent (75 : 25), then 0.22 g of a 5% palladium/carbon catalyst were added, and the reaction system was saturated with hydrogen and agitated for 1 day at the room temperature. After the reaction, the catalyst was removed by a filtration with a membrane filter of 0.25 μm , thereby recovering the reaction solution. The

solution was concentrated, then dissolved in chloroform, and re-precipitated from methanol of a 10-times amount. The obtained polymer was recovered and dried under a reduced pressure to obtain 0.68 g of a polymer. An NMR analysis conducted under conditions same as in Example 6 for specifying the structure of the obtained compound confirmed a polyhydroxyalkanoate copolymer containing units represented by a chemical formula (140) as monomer units. Also a proportion of the monomer units was confirmed as unit C by 12 mol% and unit D by 88 mol%.

[0621]

[Chemical Formula 228]



15 [0622]

An average molecular weight of the obtained polyhydroxyalkanoate was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-GEL Super HM-H, solvent: chloroform, converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 43,700$ and a weight-averaged molecular weight $M_w = 59,400$.

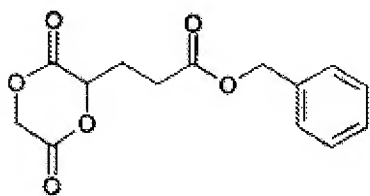
[0623]

(Example 84)

[Polyester synthesis utilizing L-3-(2-benzyloxycarbonyl)ethyl-1,4-dioxane-2,5-dione and L-lactide]

[0624]

[Chemical Formula 229]



(46)

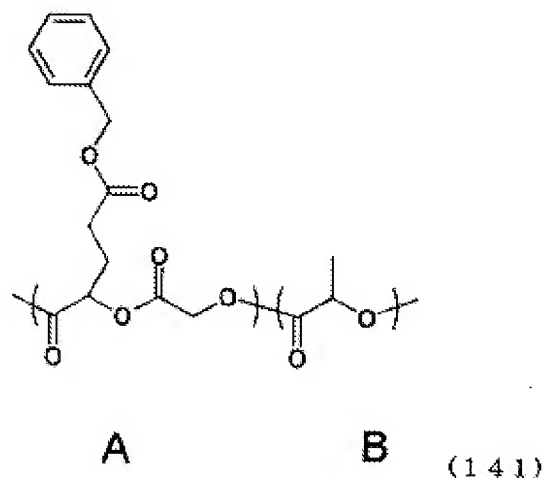
[0625]

1.11 g (4.0 mmol) of L-3-(2-benzyloxycarbonyl)ethyl-1,4-dioxane-2,5-dione synthesized in Example 79, 1.44 g (10.0 mmol) of L-lactide and 6 ml of a 0.01M toluene solution of tin octylate (tin 2-ethylhexanoate) were charged in a polymerization ampoule, then subjected to a drying for 1 hour under a reduced pressure and a nitrogen replacement, and the ampoule was sealed by fusing under a reduced pressure and heated at 150°C to execute a ring-opening polymerization. The reaction was terminated after 2 hours and the mixture was cooled. An obtained polymer was dissolved in chloroform, and was re-precipitated in methanol of a 10 times amount of that of chloroform required for dissolving. The

precipitate was recovered and dried under a reduced pressure to obtain 2.23 g of a polymer. An NMR analysis conducted under conditions same as in Example 6 for specifying the structure of the obtained polymer confirmed as a polyhydroxyalkanoate constituted of a unit represented by chemical formula (141) as the monomer. It was also confirmed that a proportion of the monomer units was unit A by 22 mol% and unit B by 78 mol%:

10 [0626]

[Chemical Formula 230]



[0627]

15 An average molecular weight of the obtained polyhydroxyalkanoate was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-GEL Super HM-H, solvent: chloroform, converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 47,300$ and a

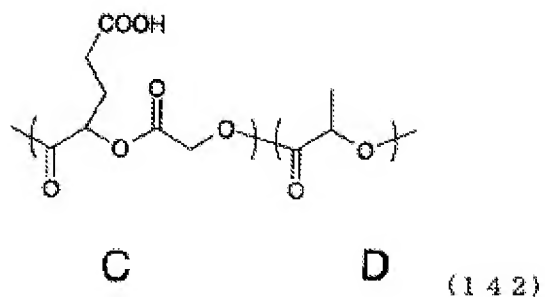
weight-averaged molecular weight $M_w = 69,100$.

[0628]

1.00 g of the obtained polyhydroxyalkanoate copolymer, represented by the chemical formula (141),
5 was dissolved in 100 ml of a dioxane-ethanol mixed solvent (75 : 25), then 0.22 g of a 5% palladium/carbon catalyst were added, and the reaction system was saturated with hydrogen and agitated for 1 day at the room temperature. After the reaction, the catalyst was
10 removed by a filtration with a membrane filter of 0.25 μm , thereby recovering the reaction solution. The solution was concentrated, then dissolved in chloroform, and re-precipitated from methanol of a 10-times amount. The obtained polymer was recovered and
15 dried under a reduced pressure to obtain 0.58 g of a polymer. An NMR analysis conducted under conditions same as in Example 6 for specifying the structure of the obtained compound confirmed a polyhydroxyalkanoate copolymer containing units represented by a chemical
20 formula (142) as monomer units. Also a proportion of the monomer units was confirmed as unit C by 22 mol% and unit D by 78 mol%.

[0629]

[Chemical Formula 231]



[0630]

An average molecular weight of the obtained polyhydroxyalkanoate was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-GEL Super HM-H, solvent: chloroform, converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 40,400$ and a weight-averaged molecular weight $M_w = 59,400$.

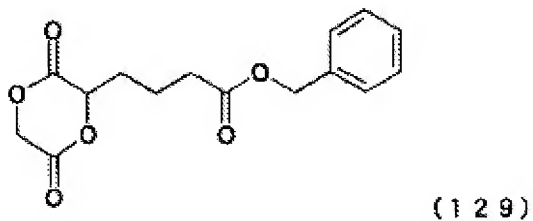
10 [0631]

(Example 85)

[Polyester synthesis utilizing L-3-(3-benzyloxycarbonyl)propyl-1,4-dioxane-2,5-dione and L-lactide]

15 [0632]

[Chemical Formula 232]

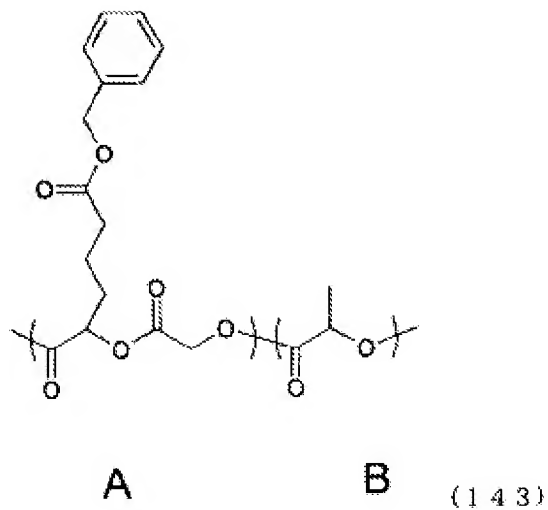


[0633]

0.58 g (2.0 mmol) of L-3-(3-benzyloxycarbonyl)propyl-1,4-dioxane-2,5-dione synthesized in Example 80, 1.44 g (10.0 mmol) of L-lactide and 5 ml of a 0.01M toluene solution of tin octylate (tin 2-ethylhexanoate) were charged in a polymerization ampoule, then subjected to a drying for 1 hour under a reduced pressure and a nitrogen replacement, and the ampoule was sealed by fusing under a reduced pressure and heated at 150°C to execute a ring-opening polymerization. The reaction was terminated after 2 hours and the mixture was cooled. An obtained polymer was dissolved in chloroform, and was re-precipitated in methanol of a 10 times amount of that of chloroform required for dissolving. The precipitate was recovered and dried under a reduced pressure to obtain 1.70 g of a polymer. An NMR analysis conducted under conditions same as in Example 6 for specifying the structure of the obtained polymer confirmed as a polyhydroxyalkanoate constituted of a unit represented by chemical formula (143) as the monomer. It was also confirmed that a proportion of the monomer units was unit A by 10 mol% and unit B by 90 mol%:

[0634]

[Chemical Formula 233]



[0635]

An average molecular weight of the obtained polyhydroxyalkanoate was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-GEL Super HM-H, solvent: chloroform, converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 49,600$ and a weight-averaged molecular weight $M_w = 65,500$.

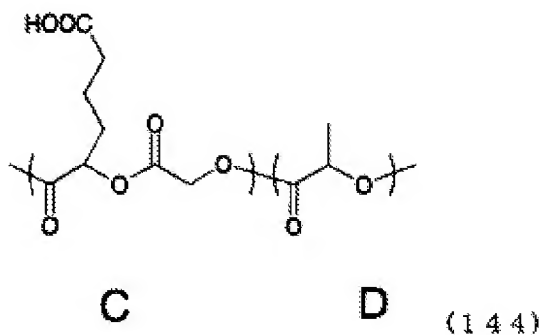
10 [0636]

1.00 g of the obtained polyhydroxyalkanoate copolymer, represented by the chemical formula (143), was dissolved in 100 ml of a dioxane-ethanol mixed solvent (75 : 25), then 0.22 g of a 5% palladium/carbon catalyst were added, and the reaction system was saturated with hydrogen and agitated for 1 day at the room temperature. After the reaction, the catalyst was removed by a filtration with a membrane filter of 0.25

μm , thereby recovering the reaction solution. The solution was concentrated, then dissolved in chloroform, and re-precipitated from methanol of a 10-times amount. The obtained polymer was recovered and
5 dried under a reduced pressure to obtain 0.73 g of a polymer. An NMR analysis conducted under conditions same as in Example 6 for specifying the structure of the obtained compound confirmed a polyhydroxyalkanoate copolymer containing units represented by a chemical
10 formula (144) as monomer units. Also a proportion of the monomer units was confirmed as unit C by 10 mol% and unit D by 90 mol%.

[0637]

[Chemical Formula 234]



15

[0638]

An average molecular weight of the obtained polyhydroxyalkanoate was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-
20 GEL Super HM-H, solvent: chloroform, converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 44,200$ and a

weight-averaged molecular weight $M_w = 64,100$.

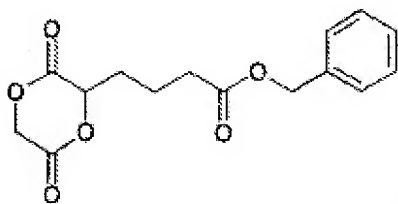
[0639]

(Example 86)

[Polyester synthesis utilizing L-3-(3-
5 benzyloxycarbonyl)propyl-1,4-dioxane-2,5-dione and L-
lactide]

[0640]

[Chemical Formula 235]



(129)

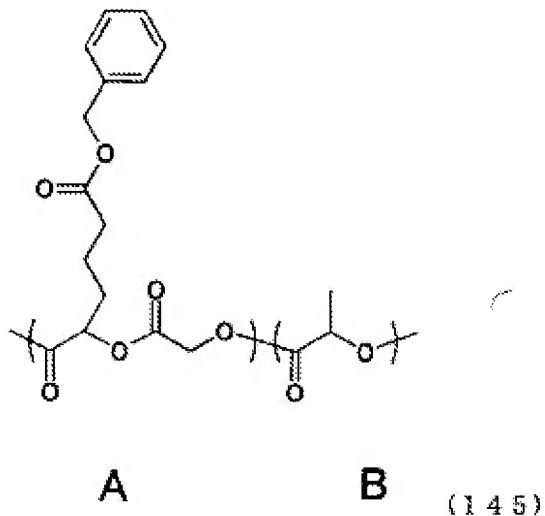
10 [0641]

1.17 g (4.0 mmol) of L-3-(3-
benzyloxycarbonyl)propyl-1,4-dioxane-2,5-dione
synthesized in Example 80, 1.44 g (10.0 mmol) of L-
lactide and 6 ml of a 0.01M toluene solution of tin
15 octylate (tin 2-ethylhexanoate) were charged in a
polymerization ampoule, then subjected to a drying for
1 hour under a reduced pressure and a nitrogen
replacement, and the ampoule was sealed by fusing under
a reduced pressure and heated at 150°C to execute a
20 ring-opening polymerization. The reaction was
terminated after 2 hours and the mixture was cooled.
An obtained polymer was dissolved in chloroform, and
was re-precipitated in methanol of a 10 times amount of

that of chloroform required for dissolving. The precipitate was recovered and dried under a reduced pressure to obtain 2.07 g of a polymer. An NMR analysis conducted under conditions same as in Example 5 6 for specifying the structure of the obtained polymer confirmed as a polyhydroxyalkanoate constituted of a unit represented by chemical formula (145) as the monomer. It was also confirmed that a proportion of the monomer units was unit A by 18 mol% and unit B by 10 82 mol%:

[0642]

[Chemical Formula 236]



[0643]

15 An average molecular weight of the obtained polyhydroxyalkanoate was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-GEL Super HM-H, solvent: chloroform, converted as

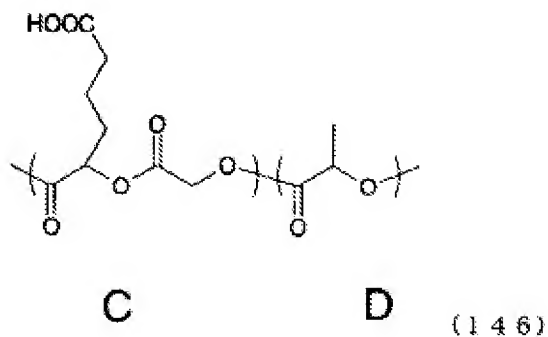
polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 49,300$ and a weight-averaged molecular weight $M_w = 69,100$.

[0644]

5 1.00 g of the obtained polyhydroxyalkanoate copolymer, represented by the chemical formula (145), was dissolved in 100 ml of a dioxane-ethanol mixed solvent (75 : 25), then 0.22 g of a 5% palladium/carbon catalyst were added, and the reaction system was
10 saturated with hydrogen and agitated for 1 day at the room temperature. After the reaction, the catalyst was removed by a filtration with a membrane filter of 0.25 μm , thereby recovering the reaction solution. The solution was concentrated, then dissolved in
15 chloroform, and re-precipitated from methanol of a 10-times amount. The obtained polymer was recovered and dried under a reduced pressure to obtain 0.65 g of a polymer. An NMR analysis conducted under conditions same as in Example 6 for specifying the structure of
20 the obtained compound confirmed a polyhydroxyalkanoate copolymer containing units represented by a chemical formula (146) as monomer units. Also a proportion of the monomer units was confirmed as unit C by 18 mol% and unit D by 82 mol%.

25 [0645]

[Chemical Formula 237]



[0646]

An average molecular weight of the obtained polyhydroxyalkanoate was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-GEL Super HM-H, solvent: chloroform, converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 42,300$ and a weight-averaged molecular weight $M_w = 59,600$.

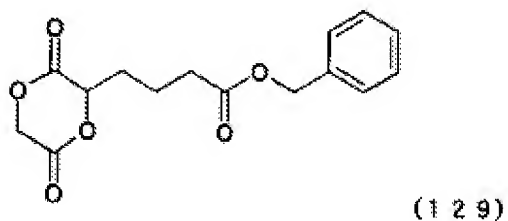
10 [0647]

(Example 87)

[Polyester synthesis utilizing L-3-(3-benzyloxycarbonyl)propyl-1,4-dioxane-2,5-dione and mandelide]

15 [0648]

[Chemical Formula 238]

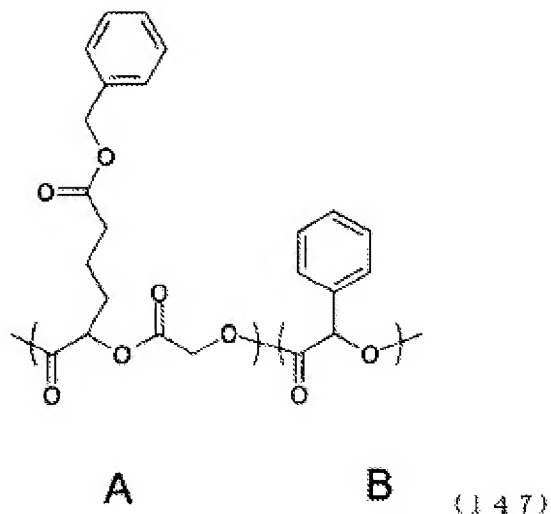


[0649]

1.17 g (4.0 mmol) of L-3-(3-benzyloxycarbonyl)propyl-1,4-dioxane-2,5-dione synthesized in Example 80, 2.68 g (10.0 mmol) of mandelide and 6 ml of a 0.01M toluene solution of tin octylate (tin 2-ethylhexanoate) were charged in a polymerization ampoule, then subjected to a drying for 1 hour under a reduced pressure and a nitrogen replacement, and the ampoule was sealed by fusing under a reduced pressure and heated at 150°C to execute a ring-opening polymerization. The reaction was terminated after 2 hours and the mixture was cooled. An obtained polymer was dissolved in chloroform, and was re-precipitated in methanol of a 10 times amount of that of chloroform required for dissolving. The precipitate was recovered and dried under a reduced pressure to obtain 2.56 g of a polymer. An NMR analysis conducted under conditions same as in Example 6 for specifying the structure of the obtained polymer confirmed as a polyhydroxyalkanoate constituted of a unit represented by chemical formula (147) as the monomer. It was also confirmed that a proportion of the monomer units was unit A by 22 mol% and unit B by 78 mol%:

[0650]

[Chemical Formula 239]



[0651]

An average molecular weight of the obtained polyhydroxyalkanoate was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-GEL Super HM-H, solvent: chloroform, converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 31,000$ and a weight-averaged molecular weight $M_w = 56,100$.

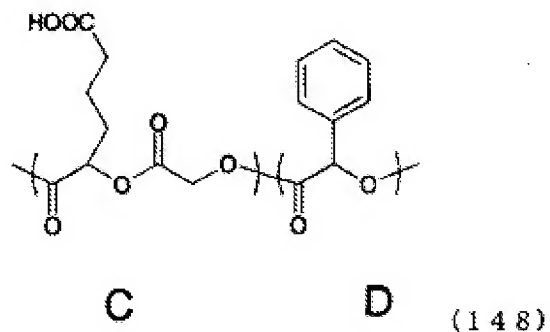
10 [0652]

1.00 g of the obtained polyhydroxyalkanoate copolymer, represented by the chemical formula (147), was dissolved in 100 ml of a dioxane-ethanol mixed solvent (75 : 25), then 0.22 g of a 5% palladium/carbon catalyst were added, and the reaction system was saturated with hydrogen and agitated for 1 day at the room temperature. After the reaction, the catalyst was removed by a filtration with a membrane filter of 0.25

μm, thereby recovering the reaction solution. The solution was concentrated, then dissolved in chloroform, and re-precipitated from methanol of a 10-times amount. The obtained polymer was recovered and
5 dried under a reduced pressure to obtain 0.71 g of a polymer. An NMR analysis conducted under conditions same as in Example 6 for specifying the structure of the obtained compound confirmed a polyhydroxyalkanoate copolymer containing units represented by a chemical
10 formula (148) as monomer units. Also a proportion of the monomer units was confirmed as unit C by 22 mol% and unit D by 78 mol%.

[0653]

[Chemical Formula 240]



15

[0654]

An average molecular weight of the obtained polyhydroxyalkanoate was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-
20 GEL Super HM-H, solvent: chloroform, converted as polystyrene). As a result, there were obtained a

number-averaged molecular weight $M_n = 27,600$ and a weight-averaged molecular weight $M_w = 49,400$.

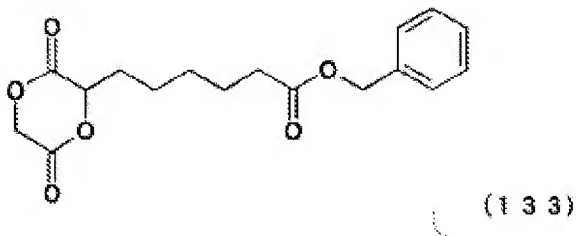
[0655]

(Example 88)

5 [Polyester synthesis utilizing 3-(5-benzyloxycarbonyl)pentyl-1,4-dioxane-2,5-dione and L-lactide]

[0656]

[Chemical Formula 241]



10

[0657]

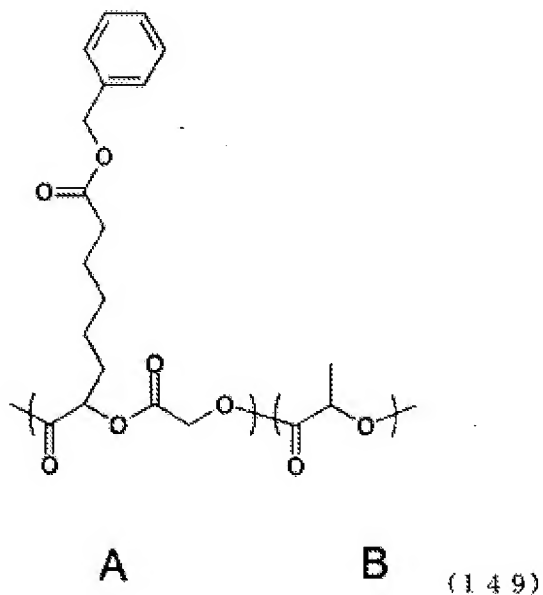
1.28 g (4.0 mmol) of 3-(5-benzyloxycarbonyl)pentyl-1,4-dioxane-2,5-dione synthesized in Example 81, 1.44 g (10.0 mmol) of L-lactide and 6 ml of a 0.01M toluene solution of tin octylate (tin 2-ethylhexanoate) were charged in a polymerization ampoule, then subjected to a drying for 1 hour under a reduced pressure and a nitrogen replacement, and the ampoule was sealed by fusing under
20 a reduced pressure and heated at 150°C to execute a ring-opening polymerization. The reaction was terminated after 2 hours and the mixture was cooled. An obtained polymer was dissolved in chloroform, and

was re-precipitated in methanol of a 10 times amount of that of chloroform required for dissolving. The precipitate was recovered and dried under a reduced pressure to obtain 1.71 g of a polymer.

5 An NMR analysis conducted under conditions same as in Example 6 for specifying the structure of the obtained polymer confirmed as a polyhydroxyalkanoate constituted of a unit represented by chemical formula (149) as the monomer. It was also confirmed that a
10 proportion of the monomer units was unit A by 14 mol% and unit B by 86 mol%:

[0658]

[Chemical Formula 242]



15 [0659]

An average molecular weight of the obtained

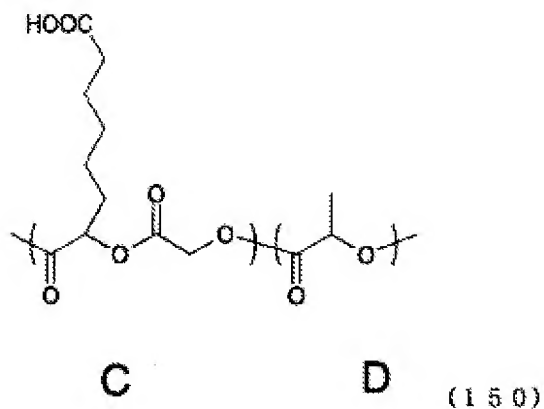
polyhydroxyalkanoate was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-GEL Super HM-H, solvent: chloroform, converted as polystyrene). As a result, there were obtained a
5 number-averaged molecular weight $M_n = 22,000$ and a weight-averaged molecular weight $M_w = 34,300$.

[0660]

1.00 g of the obtained polyhydroxyalkanoate copolymer, represented by the chemical formula (149),
10 was dissolved in 100 ml of a dioxane-ethanol mixed solvent (75 : 25), then 0.22 g of a 5% palladium/carbon catalyst were added, and the reaction system was saturated with hydrogen and agitated for 1 day at the room temperature. After the reaction, the catalyst was
15 removed by a filtration with a membrane filter of 0.25 μm , thereby recovering the reaction solution. The solution was concentrated, then dissolved in chloroform, and re-precipitated from methanol of a 10-times amount. The obtained polymer was recovered and
20 dried under a reduced pressure to obtain 0.66 g of a polymer. An NMR analysis conducted under conditions same as in Example 6 for specifying the structure of the obtained compound confirmed a polyhydroxyalkanoate copolymer containing units represented by a chemical
25 formula (150) as monomer units. Also a proportion of the monomer units was confirmed as unit C by 14 mol% and unit D by 86 mol%.

[0661]

[Chemical Formula 243]



[0662]

5 An average molecular weight of the obtained polyhydroxyalkanoate was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-GEL Super HM-H, solvent: chloroform, converted as polystyrene). As a result, there were obtained a
10 number-averaged molecular weight $M_n = 19,600$ and a weight-averaged molecular weight $M_w = 29,400$.

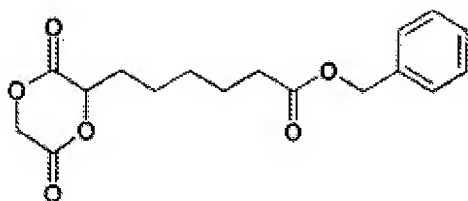
[0663]

(Example 89)

15 [Polyester synthesis utilizing 3-(5-benzyloxycarbonyl)pentyl-1,4-dioxane-2,5-dione and mandelide]

[0664]

[Chemical Formula 244]



(133)

[0665]

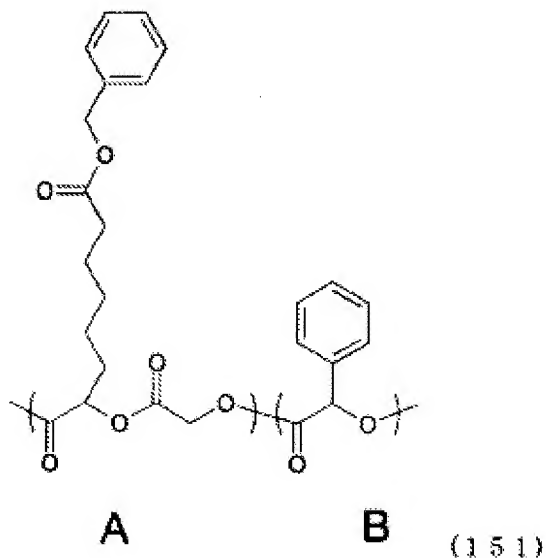
1.28 g (4.0 mmol) of 3-(5-benzyloxycarbonyl)pentyl-1,4-dioxane-2,5-dione
5 synthesized in Example 81, 2.68 g (10.0 mmol) of
mandelide and 6 ml of a 0.01M toluene solution of tin
octylate (tin 2-ethylhexanoate) were charged in a
polymerization ampoule, then subjected to a drying for
1 hour under a reduced pressure and a nitrogen
10 replacement, and the ampoule was sealed by fusing under
a reduced pressure and heated at 150°C to execute a
ring-opening polymerization. The reaction was
terminated after 2 hours and the mixture was cooled.
An obtained polymer was dissolved in chloroform, and
15 was re-precipitated in methanol of a 10 times amount of
that of chloroform required for dissolving. The
precipitate was recovered and dried under a reduced
pressure to obtain 1.90 g of a polymer.

An NMR analysis conducted under conditions same as
20 in Example 6 for specifying the structure of the
obtained polymer confirmed as a polyhydroxyalkanoate
constituted of a unit represented by chemical formula

(151) as the monomer. It was also confirmed that a proportion of the monomer units was unit A by 16 mol% and unit B by 84 mol%:

[0666]

5 [Chemical formula 245]



[0667]

An average molecular weight of the obtained polyhydroxyalkanoate was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-
10 GEL Super HM-H, solvent: chloroform, converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 18,000$ and a weight-averaged molecular weight $M_w = 31,500$.

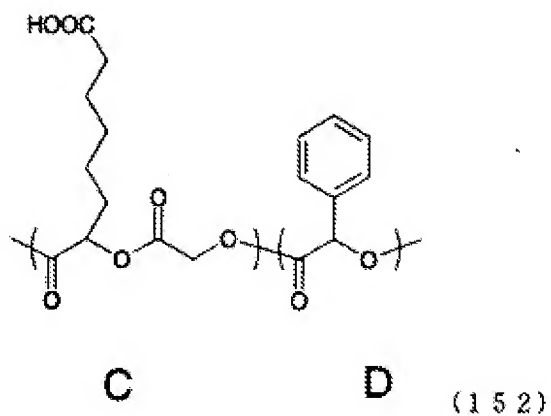
15 [0668]

1.00 g of the obtained polyhydroxyalkanoate copolymer, represented by the chemical formula (151),

was dissolved in 100 ml of a dioxane-ethanol mixed solvent (75 : 25), then 0.22 g of a 5% palladium/carbon catalyst were added, and the reaction system was saturated with hydrogen and agitated for 1 day at the room temperature. After the reaction, the catalyst was removed by a filtration with a membrane filter of 0.25 μm , thereby recovering the reaction solution. The solution was concentrated, then dissolved in chloroform, and re-precipitated from methanol of a 10- times amount. The obtained polymer was recovered and dried under a reduced pressure to obtain 0.70 g of a polymer. An NMR analysis conducted under conditions same as in Example 6 for specifying the structure of the obtained compound confirmed a polyhydroxyalkanoate copolymer containing units represented by a chemical formula (152) as monomer units. Also a proportion of the monomer units was confirmed as unit C by 16 mol% and unit D by 84 mol%.

[0669]

[Chemical Formula 246]



[0670]

An average molecular weight of the obtained polyhydroxyalkanoate was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-GEL Super HM-H, solvent: chloroform, converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 17,600$ and a weight-averaged molecular weight $M_w = 31,900$.

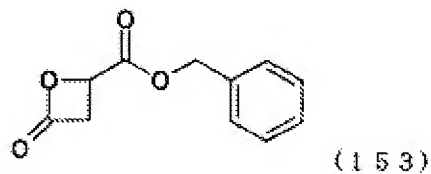
10 [0671]

(Example 90)

[Polyester synthesis utilizing β -malolactone benzyl ester and L-lactide]

[0672]

15 [Chemical Formula 247]

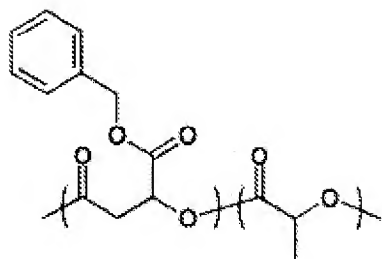


[0673]

β -malolactone benzyl ester represented by chemical formula (153) was prepared by the same method as in USP No. 4,265,247. 0.82 g (4.0 mmol) of β -malolactone benzyl ester, 1.44 g (10.0 mmol) of L-lactide, 20 μ l of a 2M toluene solution of diethyl zinc and 11.2 ml of a 0.01M toluene solution of p-tert-butylbenzyl alcohol were charged in a polymerization ampoule, then subjected to a drying for 1 hour under a reduced pressure and a nitrogen replacement, and the ampoule was sealed by fusing under a reduced pressure and heated at 150°C to execute a ring-opening polymerization. The reaction was terminated after 10 hours and the mixture was cooled. An obtained polymer was dissolved in chloroform, and was re-precipitated in methanol of a 10 times amount of that of chloroform required for dissolving. The precipitate was recovered and dried under a reduced pressure to obtain 1.09 g of a polymer. An NMR analysis conducted under conditions same as in Example 6 for specifying the structure of the obtained polymer confirmed as a polyhydroxyalkanoate constituted of a unit represented by chemical formula (154) as the monomer. It was also confirmed that a proportion of the monomer units was unit A by 8 mol% and unit B by 92 mol%:

[0674]

[Chemical Formula 248]



A **B** (154)

[0675]

An average molecular weight of the obtained polyhydroxyalkanoate was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-GEL Super HM-H, solvent: chloroform, converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 8,200$ and a weight-averaged molecular weight $M_w = 12,500$.

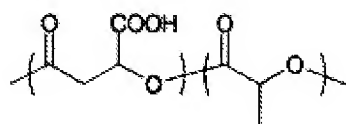
10 [0676]

1.00 g of the obtained polyhydroxyalkanoate copolymer, represented by the chemical formula (154), was dissolved in 100 ml of a dioxane-ethanol mixed solvent (75 : 25), then 0.22 g of a 5% palladium/carbon catalyst were added, and the reaction system was saturated with hydrogen and agitated for 1 day at the room temperature. After the reaction, the catalyst was removed by a filtration with a membrane filter of 0.25 μm , thereby recovering the reaction solution. The solution was concentrated, then dissolved in chloroform, and re-precipitated from methanol of a 10-

times amount. The obtained polymer was recovered and dried under a reduced pressure to obtain 0.76 g of a polymer. An NMR analysis conducted under conditions same as in Example 6 for specifying the structure of the obtained compound confirmed a polyhydroxyalkanoate copolymer containing units represented by a chemical formula (155) as monomer units. Also a proportion of the monomer units was confirmed as unit C by 8 mol% and unit D by 92 mol%.

10 [0677]

[Chemical Formula 249]



C D (155)

[0678]

An average molecular weight of the obtained polyhydroxyalkanoate was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-GEL Super HM-H, solvent: chloroform, converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 7,600$ and a weight-averaged molecular weight $M_w = 11,800$.

20 [0679]

(Example 91)

[Polyester synthesis utilizing β -malolactone

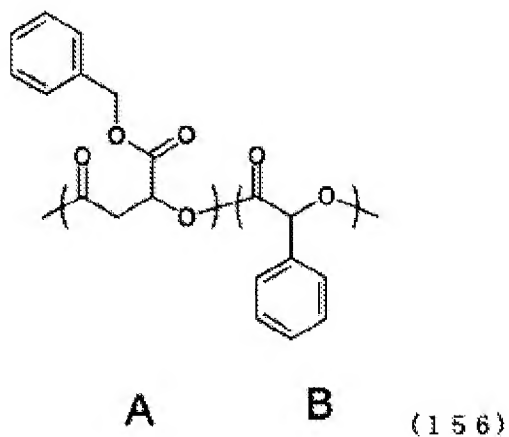
benzyl ester and mandelide]

0.82 g (4.0 mmol) of β -malolactone benzyl ester,
2.68 g (10.0 mmol) of mandelide, 28 μ l of a 2M toluene
solution of diethyl zinc and 11.2 ml of a 0.01M toluene
5 solution of p-tert-butylbenzyl alcohol were charged in
a polymerization ampoule, then subjected to a drying
for 1 hour under a reduced pressure and a nitrogen
replacement, and the ampoule was sealed by fusing under
a reduced pressure and heated at 150°C to execute a
10 ring-opening polymerization. The reaction was
terminated after 10 hours and the mixture was cooled.
An obtained polymer was dissolved in chloroform, and
was re-precipitated in methanol of a 10 times amount of
that of chloroform required for dissolving. The
15 precipitate was recovered and dried under a reduced
pressure to obtain 1.27 g of a polymer.

An NMR analysis conducted under conditions same as
in Example 6 for specifying the structure of the
obtained polymer confirmed as a polyhydroxyalkanoate
20 constituted of a unit represented by chemical formula
(156) as the monomer. It was also confirmed that a
proportion of the monomer units was unit A by 8 mol%
and unit B by 92 mol%:

[0680]

25 [Chemical Formula 250]



[0681]

An average molecular weight of the obtained polyhydroxyalkanoate was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-GEL Super HM-H, solvent: chloroform, converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 6,500$ and a weight-averaged molecular weight $M_w = 11,200$.

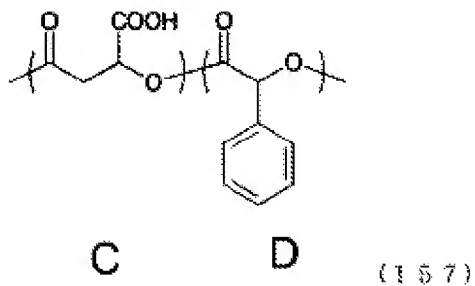
10 [0682]

1.00 g of the obtained polyhydroxyalkanoate copolymer, represented by the chemical formula (156), was dissolved in 100 ml of a dioxane-ethanol mixed solvent (75 : 25), then 0.22 g of a 5% palladium/carbon catalyst were added, and the reaction system was saturated with hydrogen and agitated for 1 day at the room temperature. After the reaction, the catalyst was removed by a filtration with a membrane filter of 0.25 μm , thereby recovering the reaction solution. The

solution was concentrated, then dissolved in chloroform, and re-precipitated from methanol of a 10-times amount. The obtained polymer was recovered and dried under a reduced pressure to obtain 0.81 g of a polymer. An NMR analysis conducted under conditions same as in Example 6 for specifying the structure of the obtained compound confirmed a polyhydroxyalkanoate copolymer containing units represented by a chemical formula (157) as monomer units. Also a proportion of the monomer units was confirmed as unit C by 8 mol% and unit D by 92 mol%.

[0683]

[Chemical Formula 251]



15 [0684]

An average molecular weight of the obtained polyhydroxyalkanoate was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-GEL Super HM-H, solvent: chloroform, converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 6,400$ and a

weight-averaged molecular weight $M_w = 10,900$.

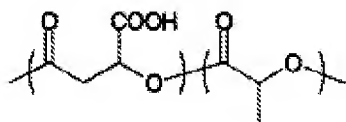
[0685]

(Example 92)

Condensation reaction of a polyhydroxyalkanoate
5 constituted of a unit represented by chemical formula
(155) synthesized in Example 90 with 2-
aminobenzenesulfonic acid phenyl ester

[0686]

[Chemical Formula 252]



C D (155)

10

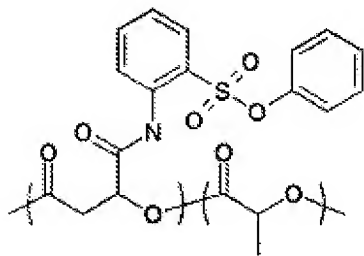
[0687]

In a nitrogen atmosphere, 0.40 g of polymer
synthesized with polyhydroxyalkanoate copolymer (C: 8
mol%, D: 92 mol%) obtained in Example 90 and
15 constituted of a unit represented by chemical formula
(155) and 0.53 g of 2-aminobenzenesulfonic acid phenyl
ester were placed in a 100-ml three-necked flask,
agitated with 15.0 ml of pyridine, further added with
1.11 ml of triphenyl phosphite and heated for 6 hours
20 at 120°C. After the reaction, the polymer was
recovered by a re-precipitation in 150 ml of ethanol.
The obtained polymer was washed with 1N hydrochloric
acid for 1 day, then washed by an agitation in water

for 1 day and dried under a reduced pressure to obtain
0.36 g of a polymer. The structure of the obtained
polymer was analyzed by ^1H -NMR (FT-NMR: Bruker DPX 400,
resonance frequency: 400 MHz, measured species: ^1H ,
5 solvent: deuterized DMSO, temperature: room
temperature) and a Fourier transformed infrared
absorption (FT-IR) spectrum (Nicolet AVATAR 360FT-IR).
The IR measurement showed a decrease of a peak at 1695 cm^{-1}
 cm^{-1} attributable to a carboxylic acid, and a new peak
10 at 1658 cm^{-1} attributable to an amide group.

A result of ^1H -NMR confirmed, by a shift in a peak
resulting from an aromatic ring of the 2-
aminobenzenesulfonic acid phenyl ester structure, that
the polymer was a polyhydroxyalkanoate containing units
15 represented by chemical formula (158) as monomer units.
[0688]

[Chemical Formula 253]



E

F

(158)

[0689]

20 It was also confirmed that a proportion of the
units of the polyhydroxyalkanoate represented by

chemical formula (158) was a copolymer as unit E by 8 mol% and unit F by 92 mol%. An average molecular weight of the obtained polymer was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8120, column:

5 Polymer Laboratories PLgel 5 μ MIXED-C, solvent: DMF/LiBr 0.1 % (w/v), converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 7,300$ and a weight-averaged molecular weight $M_w = 11,500$.

10 [0690]

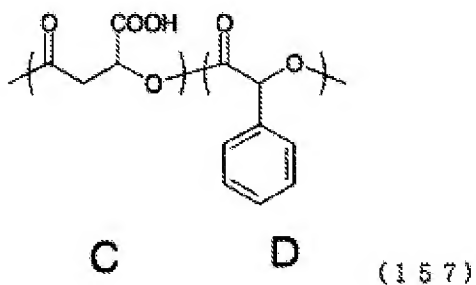
(Example 93)

Condensation reaction of a polyhydroxyalkanoate constituted of a unit represented by chemical formula (157) synthesized in Example 91 with 2-amino-2-

15 methylpropanesulfonic acid

[0691]

[Chemical Formula 254]



[0692]

20 In a nitrogen atmosphere, 0.40 g of polymer synthesized with polyhydroxyalkanoate copolymer (C: 8 mol%, D: 92 mol%) obtained in Example 91 and

constituted of a unit represented by chemical formula (157) and 0.18 g of 2-amino-2-methylpropanesulfonic acid were placed in a 100-ml three-necked flask, agitated with 15.0 ml of pyridine, further added with 0.63 ml of triphenyl phosphite and heated for 6 hours at 120°C. After the reaction, the polymer was recovered by a re-precipitation in 150 ml of ethanol. The obtained polymer was washed with 1N hydrochloric acid for 1 day, then washed by an agitation in water for 1 day and dried under a reduced pressure to obtain 0.32 g of a polymer.

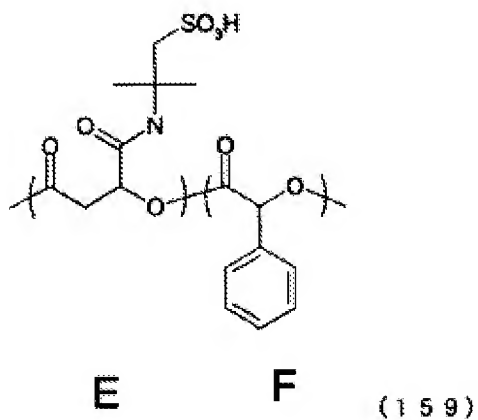
[0693]

The structure of the obtained polymer was analyzed by ^1H -NMR (FT-NMR: Bruker DPX 400, resonance frequency: 400 MHz, measured species: ^1H , solvent: deuterized DMSO, temperature: room temperature) and a Fourier transformed infrared absorption (FT-IR) spectrum (Nicolet AVATAR 360FT-IR). The IR measurement showed a decrease of a peak at 1695 cm^{-1} attributable to a carboxylic acid, and a new peak at 1658 cm^{-1} attributable to an amide group.

A result of ^1H -NMR confirmed, by a shift in a peak resulting from a methylene of the 2-amino-2-methylpropanesulfonic acid structure, that the polymer was a polyhydroxyalkanoate containing units represented by chemical formula (159) as monomer units.

[0694]

[Chemical Formula 255]



[0695]

It was also confirmed that a proportion of the
5 units of the polyhydroxyalkanoate represented by
chemical formula (159) was a copolymer as unit E by 8
mol% and unit F by 92 mol%. An average molecular
weight of the obtained polymer was evaluated by gel
permeation chromatography (GPC: Tosoh HLC-8120, column:
10 Polymer Laboratories PLgel 5 μ MIXED-C, solvent:
DMF/LiBr 0.1 %(w/v), converted as polystyrene). As a
result, there were obtained a number-averaged molecular
weight $M_n = 6,000$ and a weight-averaged molecular
weight $M_w = 10,400$.

15 [0696]

(Example 94)

[0697]

[Chemical Formula 256]



(160)

[0698]

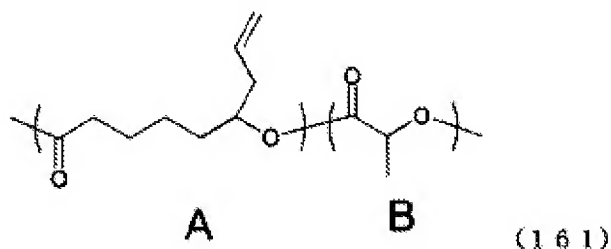
[Polyester synthesis utilizing 7-(2-propenyl)-2-oxepanone represented by chemical formula (160) and L-lactide]

0.31 g (2.0 mmol) of 7-(2-propenyl)-2-oxepanone, 1.15 g (8.0 mmol) of L-lactide, 20 µl of a 2M toluene solution of di-iso-propyl zinc and 8 ml of a 0.01M toluene solution of p-tert-butylbenzyl alcohol were charged in a polymerization ampoule, then subjected to a drying for 1 hour under a reduced pressure and a nitrogen replacement, and the ampoule was sealed by fusing under a reduced pressure and heated at 150°C to execute a ring-opening polymerization. The reaction was terminated after 10 hours and the mixture was cooled. An obtained polymer was dissolved in chloroform, and was re-precipitated in methanol of a 10 times amount of that of chloroform required for dissolving. The precipitate was recovered and dried under a reduced pressure to obtain 1.09 g of a polymer. An NMR analysis conducted under conditions same as in Example 6 for specifying the structure of the obtained polymer confirmed as a polyhydroxyalkanoate constituted of a unit represented by chemical formula (161) as the

monomer. It was also confirmed that a proportion of the monomer units was unit A by 11 mol% and unit B by 89 mol%:

[0699]

5 [Chemical Formula 257]



[0700]

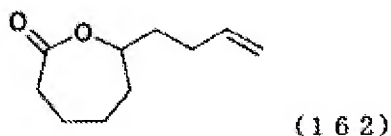
An average molecular weight of the obtained polyhydroxyalkanoate was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-GEL Super HM-H, solvent: chloroform, converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 56,400$ and a weight-averaged molecular weight $M_w = 91,400$.

15 [0701]

(Example 95)

[0702]

[Chemical Formula 258]



20 [0703]

[Polyester synthesis utilizing 7-(3-butenyl)-2-oxepanone represented by chemical formula (162) and L-lactide]

0.34 g (2.0 mmol) of 7-(3-butenyl)-2-oxepanone,
5 1.15 g (8.0 mmol) of L-lactide, 20 µl of a 2M toluene
solution of di-iso-propyl zinc and 8 ml of a 0.01M
toluene solution of p-tert-butylbenzyl alcohol were
charged in a polymerization ampoule, then subjected to
a drying for 1 hour under a reduced pressure and a
10 nitrogen replacement, and the ampoule was sealed by
fusing under a reduced pressure and heated at 150°C to
execute a ring-opening polymerization. The reaction
was terminated after 10 hours and the mixture was
cooled. An obtained polymer was dissolved in
15 chloroform, and was re-precipitated in methanol of a 10
times amount of that of chloroform required for
dissolving. The precipitate was recovered and dried
under a reduced pressure to obtain 1.05 g of a polymer.
An NMR analysis conducted under conditions same as in
20 Example 6 for specifying the structure of the obtained
polymer confirmed as a polyhydroxyalkanoate constituted
of a unit represented by chemical formula (163) as the
monomer. It was also confirmed that a proportion of
the monomer units was unit A by 8 mol% and unit B by 92
25 mol%:

[0704]

[Chemical Formula 259]

An average molecular weight of the obtained polyhydroxyalkanoate was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-GEL Super HM-H, solvent: chloroform, converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 43,500$ and a weight-averaged molecular weight $M_w = 67,400$.

(Example 96)

15 [0707]

C=CCCCOC(=O)C(C)OC(=O)CCCCCCC(=O)OCC

A B

(161)

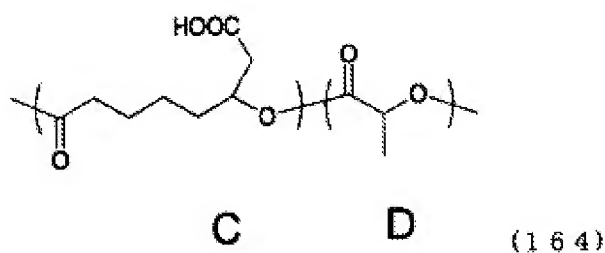
[0708]

0.50 g of polyhydroxyalkanoate copolymer (A: 11 mol%, B: 89 mol%) obtained in Example 94 and constituted of a unit represented by chemical formula (161) were placed in an eggplant-shaped flask, and dissolved by adding 30 ml of acetone. The solution was placed in an ice bath and agitated while added 5 ml of acetic acid and 0.54 g of 18-crown-6-ether. Then 0.43 g of potassium permanganate was slowly added in the ice bath and the mixture was agitated for 2 hours in the ice bath and further 18 hours at the room temperature. After the reaction, 60 ml of ethyl acetate and further 45 ml of water were added. Next, sodium hydrogen sulfite was added until overacidity was removed. Then, the liquid factor was made to pH = 1 by 1.0 N of hydrochloric acid. The organic layer was separated. The organic layer was recovered and washed three times with 1.0 N of hydrochloric acid. After recovering the organic layer, the solvent was distilled off to recover a crude polymer. Next, the polymer was recovered after cleaning with 50 ml of water and 50 ml of methanol, and then cleaning three times with 50 ml of water. It was then dissolved in THF, and was re-precipitated in methanol of a 50-times amount of that of THF required for dissolving. The precipitate was recovered and dried under a reduced pressure to obtain 0.45 g of polymer. An NMR analysis conducted under conditions

same as in Example 6 for specifying the structure of the obtained polymer confirmed a polyhydroxyalkanoate containing units represented by chemical formula (164) as monomer units.

5 [0709]

[Chemical Formula 261]



[0710]

An average molecular weight of the obtained
10 polyhydroxyalkanoate was evaluated by gel permeation
chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-
GEL Super HM-H, solvent: chloroform, converted as
polystyrene). As a result, there were obtained a
number-averaged molecular weight $M_n = 41,300$ and a
15 weight-averaged molecular weight $M_w = 67,700$.

Furthermore, in order to calculate the units of
the obtained polyhydroxyalkanoate, the calculation was
made by methyl esterification of the carboxyl group at
the end of the side chain of the polyhydroxyalkanoate
20 using trimethylsilyl diazomethane. 30 mg of the
targeted polyhydroxyalkanoate were placed in a 100-ml
eggplant-shaped flask and dissolved by adding 2.1 ml of

chloroform and 0.7 ml of methanol. Then 0.5 ml of a 2 mol/L hexane solution of trimethylsilyl diazomethane were added and the mixture was agitated for 1 hour at the room temperature. After the reaction, the solvent was distilled off to recover the polymer. The polymer was washed with 50 ml of methanol, then recovered, and dried under a reduced pressure to obtain 29 mg of polyhydroxyalkanoate.

[0711]

An NMR analysis conducted under conditions same as in Example 6 confirmed that a proportion of the units of the polyhydroxyalkanoate represented by chemical formula (164) was a copolymer as unit C by 11 mol% and unit D by 89 mol%.

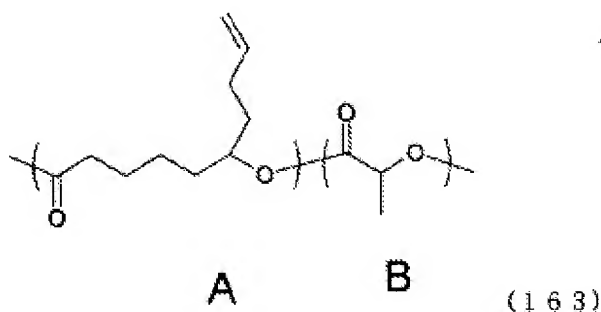
[0712]

(Example 97)

Oxidation reaction of a polyhydroxyalkanoate constituted of a unit represented by chemical formula (163) synthesized in Example 95

[0713]

[Chemical Formula 262]



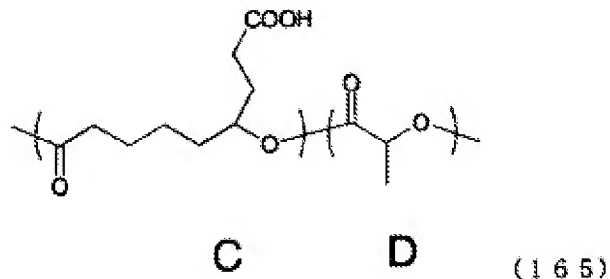
[0714]

0.50 g of polyhydroxyalkanoate copolymer (A: 8 mol%, B: 92 mol%) obtained in Example 95 and
5 constituted of a unit represented by chemical formula (163) were placed in an eggplant-shaped flask, and dissolved by adding 30 ml of acetone. The solution was placed in an ice bath and agitated while added 5 ml of acetic acid and 0.40 g of 18-crown-6-ether. Then 0.32
10 g of potassium permanganate was slowly added in the ice bath and the mixture was agitated for 2 hours in the ice bath and further 18 hours at the room temperature. After the reaction, 60 ml of ethyl acetate and further 45 ml of water were added. Next, sodium hydrogen
15 sulfite was added until overacidity was removed. Then, the liquid factor was made to pH = 1 by 1.0 N of hydrochloric acid. The organic layer was separated. The organic layer was recovered and washed three times with 1.0 N of hydrochloric acid. After recovering the
20 organic layer, the solvent was distilled off to recover a crude polymer. Next, the polymer was recovered after

cleaning with 50 ml of water and 50 ml of methanol, and then cleaning three times with 50 ml of water. It was then dissolved in THF, and was re-precipitated in methanol of a 50-times amount of that of THF required
5 for dissolving. The precipitate was recovered and dried under a reduced pressure to obtain 0.44 g of polymer. An NMR analysis conducted under conditions same as in Example 6 for specifying the structure of the obtained polymer confirmed a polyhydroxyalkanoate
10 containing units represented by chemical formula (165) as monomer units.

[0715]

[Chemical Formula 263]



15 [0716]

An average molecular weight of the obtained polyhydroxyalkanoate was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-GEL Super HM-H, solvent: chloroform, converted as
20 polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 37,500$ and a weight-averaged molecular weight $M_w = 59,600$.

Furthermore, in order to calculate the units of the obtained polyhydroxyalkanoate, the calculation was made by methyl esterification of the carboxyl group at the end of the side chain of the polyhydroxyalkanoate using trimethylsilyl diazomethane. 30 mg of the targeted polyhydroxyalkanoate were placed in a 100-ml eggplant-shaped flask and dissolved by adding 2.1 ml of chloroform and 0.7 ml of methanol. Then 0.5 ml of a 2 mol/L hexane solution of trimethylsilyl diazomethane were added and the mixture was agitated for 1 hour at the room temperature. After the reaction, the solvent was distilled off to recover the polymer. The polymer was washed with 50 ml of methanol, then recovered, and dried under a reduced pressure to obtain 28 mg of polyhydroxyalkanoate.

[0717]

An NMR analysis conducted under conditions same as in Example 6 confirmed that a proportion of the units of the polyhydroxyalkanoate represented by chemical formula (165) was a copolymer as unit C by 8 mol% and unit D by 92 mol%.

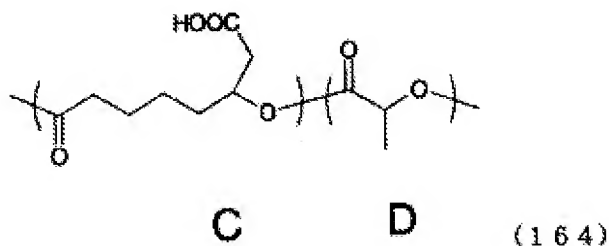
[0718]

(Example 98)

Condensation reaction of a polyhydroxyalkanoate constituted of a unit represented by chemical formula (164) synthesized in Example 96 with 2-aminobenzenesulfonic acid phenyl ester

[0719]

[Chemical Formula 264]



[0720]

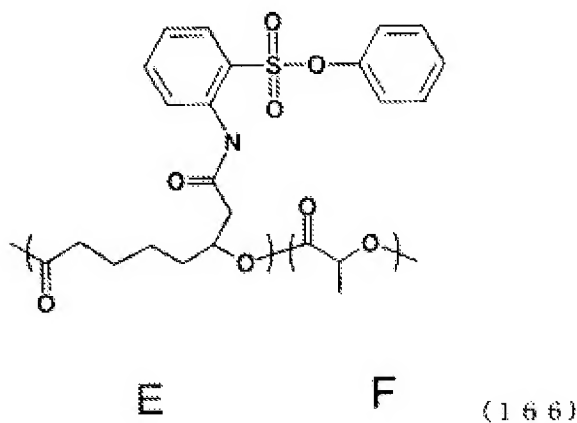
5 In a nitrogen atmosphere, 0.40 g of polymer
synthesized with polyhydroxyalkanoate copolymer (C: 11
mol%, D: 89 mol%) obtained in Example 96 and
constituted of a unit represented by chemical formula
(164) and 0.66 g of 2-aminobenzenesulfonic acid phenyl
10 ester were placed in a 100-ml three-necked flask,
agitated with 15.0 ml of pyridine, further added with
1.38 ml of triphenyl phosphite and heated for 6 hours
at 120°C. After the reaction, the polymer was
recovered by a re-precipitation in 150 ml of ethanol.
15 The obtained polymer was washed with 1N hydrochloric
acid for 1 day, then washed by an agitation in water
for 1 day and dried under a reduced pressure to obtain
0.36 g of a polymer. The structure of the obtained
polymer was analyzed by ¹H-NMR (FT-NMR: Bruker DPX 400,
20 resonance frequency: 400 MHz, measured species: ¹H,
solvent: deuterized DMSO, temperature: room
temperature) and a Fourier transformed infrared

absorption (FT-IR) spectrum (Nicolet AVATAR 360FT-IR). The IR measurement showed a decrease of a peak at 1695 cm^{-1} attributable to a carboxylic acid, and a new peak at 1658 cm^{-1} attributable to an amide group.

5 A result of ^1H -NMR confirmed, by a shift in a peak resulting from an aromatic ring of the 2-aminobenzenesulfonic acid structure, that the polymer was a polyhydroxyalkanoate containing units represented by chemical formula (166) as monomer units.

10 [0721]

[Chemical Formula 265]



[0722]

15 It was also confirmed that a proportion of the units of the polyhydroxyalkanoate represented by chemical formula (166) was a copolymer as unit E by 11 mol% and unit F by 89 mol%. An average molecular weight of the obtained polymer was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8120, column:

Polymer Laboratories PLgel 5 μ MIXED-C, solvent:
DMF/LiBr 0.1 %(w/v), converted as polystyrene). As a
result, there were obtained a number-averaged molecular
weight $M_n = 41,300$ and a weight-averaged molecular
5 weight $M_w = 67,700$.

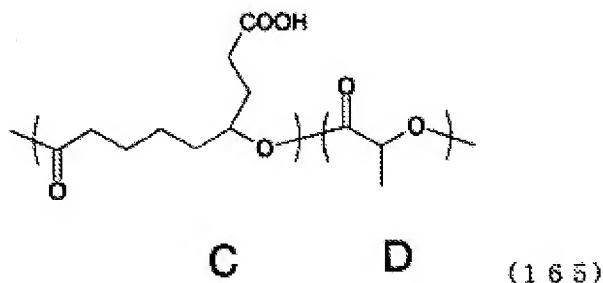
[0723]

(Example 99)

Condensation reaction of a polyhydroxyalkanoate
constituted of a unit represented by chemical formula
10 (165) synthesized in Example 97 with 2-amino-2-
methylpropanesulfonic acid

[0724]

[Chemical Formula 266]



15 [0725]

In a nitrogen atmosphere, 0.40 g of polymer
synthesized with polyhydroxyalkanoate copolymer (C: 8
mol%, D: 92 mol%) obtained in Example 97 and
constituted of a unit represented by chemical formula
20 (165) and 0.30 g of 2-amino-2-methylpropanesulfonic
acid were placed in a 100-ml three-necked flask,
agitated with 15.0 ml of pyridine, further added with

1.03 ml of triphenyl phosphite and heated for 6 hours
at 120°C. After the reaction, the polymer was
recovered by a re-precipitation in 150 ml of ethanol.
The obtained polymer was washed with 1N hydrochloric
5 acid for 1 day, then washed by an agitation in water
for 1 day and dried under a reduced pressure to obtain
0.32 g of a polymer.

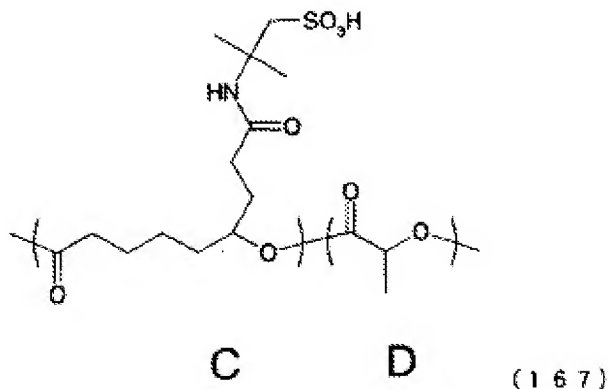
[0726]

The structure of the obtained polymer was analyzed
10 by ^1H -NMR (FT-NMR: Bruker DPX 400, resonance frequency:
400 MHz, measured species: ^1H , solvent: deuterized
DMSO, temperature: room temperature) and a Fourier
transformed infrared absorption (FT-IR) spectrum
(Nicolet AVATAR 360FT-IR). The IR measurement showed a
15 decrease of a peak at 1695 cm^{-1} attributable to a
carboxylic acid, and a new peak at 1658 cm^{-1}
attributable to an amide group.

A result of ^1H -NMR confirmed, by a shift in a peak
resulting from an aromatic ring of the 2-amino-2-
20 methylpropanesulfonic acid structure, that the polymer
was a polyhydroxyalkanoate containing units represented
by chemical formula (167) as monomer units.

[0727]

[Chemical Formula 267]



[0728]

It was also confirmed that a proportion of the units of the polyhydroxyalkanoate represented by chemical formula (167) was a copolymer as unit E by 8 mol% and unit F by 92 mol%. An average molecular weight of the obtained polymer was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8120, column: Polymer Laboratories PLgel 5 μ MIXED-C, solvent: DMF/LiBr 0.1 % (w/v), converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 37,500$ and a weight-averaged molecular weight $M_w = 59,600$.

[0729]

(Example 100)

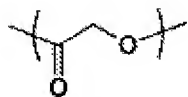
[Polyester synthesis utilizing glycolide]

11.61 g (100.0 mmol) of glycolide, 4 ml of a 0.1M toluene solution of tin octylate (tin 2-ethylhexanoate) and 4 ml of a 0.01M toluene solution of p-tert-butylbenzyl alcohol were charged in a polymerization

ampoule, then subjected to a drying for 1 hour under a reduced pressure and a nitrogen replacement, and the ampoule was sealed by fusing under a reduced pressure and heated at 150°C to execute a ring-opening polymerization. The reaction was terminated after 10 hours and the mixture was cooled. An obtained polymer was dissolved in chloroform, and was re-precipitated in methanol of a 10 times amount of that of chloroform required for dissolving. The precipitate was recovered and dried under a reduced pressure to obtain 9.63 g of a polymer. An NMR analysis conducted under conditions same as in Example 6 for specifying the structure of the obtained polymer confirmed as a polyhydroxyalkanoate copolymer containing a unit represented by below chemical formula (178) as the monomer unit.

[0730]

[Chemical Formula 268]



B

(178)

20 [0731]

An average molecular weight of the obtained polyhydroxyalkanoate was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-GEL Super HM-H, solvent: chloroform, converted as

polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 73,000$ and a weight-averaged molecular weight $M_w = 130,100$.

[0732]

5 (Example 101)

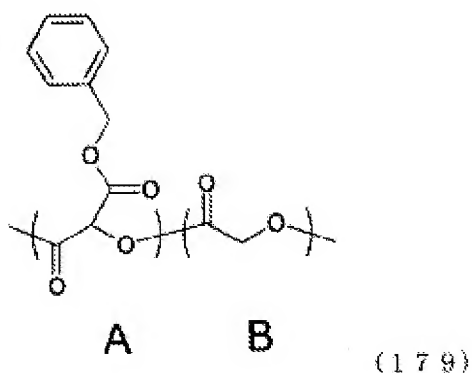
2.00 g of polyhydroxyalkanoate obtained in Example 100 and constituted of a unit represented by the chemical formula (178) were placed in an eggplant-shaped flask, and dissolved by adding 100 ml of THF.

10 The solution was placed under a nitrogen atmosphere and agitated at -78°C . Then 18.9 ml of a 2M THF solution of lithium diisopropylamide were slowly added and the mixture was agitated for 30 minutes at -78°C . Then 12.86 g of benzyl chloroformate were added and the
15 mixture was agitated for 30 minutes at the room temperature. After the reaction, the reaction mixture was poured into 400 ml of an aqueous solution of ammonium chloride, then 200 ml of dichloromethane were added and the organic layer was separated. The organic
20 layer was recovered after washing three times with 100 ml of water, and the solvent was distilled off to recover a crude polymer. It was then dissolved in 12 ml of THF, and was re-precipitated in methanol of a 50-times amount of that of THF required for dissolving.
25 The precipitate was recovered and dried under a reduced pressure to obtain 1.22 g of polymer. An NMR analysis conducted under conditions same as in Example 6 for

specifying the structure of the obtained polymer confirmed a polyhydroxyalkanoate containing units represented by a chemical formula (179) as monomer units. It was also confirmed that a proportion of the
5 monomer units was unit A by 8 mol% and unit B by 92 mol%.

[0733]

[Chemical Formula 269]



10 [0734]

An average molecular weight of the obtained polyhydroxyalkanoate was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-GEL Super HM-H, solvent: chloroform, converted as
15 polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 42,100$ and a weight-averaged molecular weight $M_w = 85,500$.

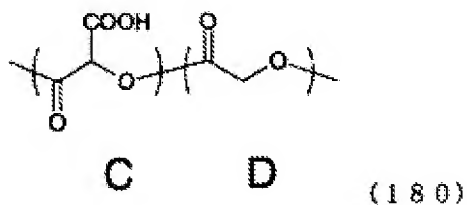
[0735]

1.00 g of the obtained polyhydroxyalkanoate
20 copolymer, represented by the chemical formula (179), was dissolved in 100 ml of a dioxane-ethanol mixed

solvent (75 : 25), then 0.22 g of a 5% palladium/carbon catalyst were added, and the reaction system was saturated with hydrogen and agitated for 1 day at the room temperature. After the reaction, the catalyst was removed by a filtration with a membrane filter of 0.25 μm , thereby recovering the reaction solution. The solution was concentrated, then dissolved in chloroform, and re-precipitated from methanol of a 10-times amount. The obtained polymer was recovered and dried under a reduced pressure to obtain 0.60 g of a polymer. An NMR analysis conducted under conditions same as in Example 6 for specifying the structure of the obtained compound confirmed a polyhydroxyalkanoate copolymer containing units represented by a chemical formula (180) as monomer units. Also a proportion of the monomer units was confirmed as unit C by 8 mol% and unit D by 92 mol%.

[0736]

[Chemical Formula 270]



20

[0737]

Also an average molecular weight of the obtained polyhydroxyalkanoate was evaluated by gel permeation

chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-GEL Super HM-H, solvent: chloroform, converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 37,400$ and a
5 weight-averaged molecular weight $M_w = 78,500$.
[0738]

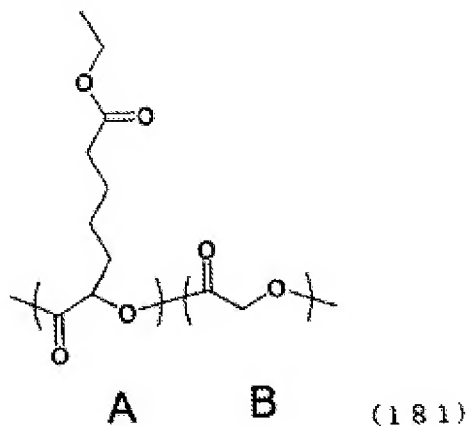
(Example 102)

2.00 g of polyhydroxyalkanoate obtained in Example 100 and constituted of a unit represented by the
10 chemical formula (178) were placed in an eggplant-shaped flask, and dissolved by adding 100 ml of THF. The solution was placed under a nitrogen atmosphere and agitated at -78°C . Then 18.9 ml of a 2M THF solution of lithium diisopropylamide were slowly added and the
15 mixture was agitated for 30 minutes at -78°C . Then 14.41 g of ethyl 5-bromovalerate were added and the mixture was agitated for 30 minutes at the room temperature. After the reaction, the reaction mixture was poured into 400 ml of an aqueous solution of
20 ammonium chloride, then 200 ml of dichloromethane were added and the organic layer was separated. The organic layer was recovered after washing three times with 100 ml of water, and the solvent was distilled off to recover a crude polymer. It was then dissolved in 12
25 ml of THF, and was re-precipitated in methanol of a 50-times amount of that of THF required for dissolving. The precipitate was recovered and dried under a reduced

pressure to obtain 1.31 g of polymer. An NMR analysis conducted under conditions same as in Example 6 for specifying the structure of the obtained polymer confirmed a polyhydroxyalkanoate containing units represented by a chemical formula (181) as monomer units. It was also confirmed that a proportion of the monomer units was unit A by 9 mol% and unit B by 91 mol%.

[0739]

10 [Chemical Formula 271]



[0740]

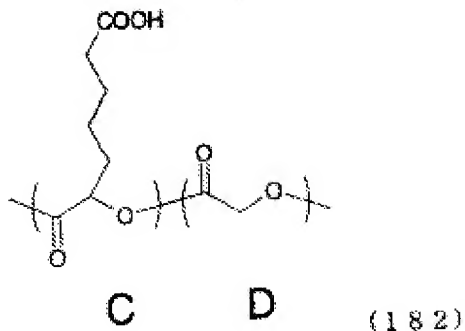
An average molecular weight of the obtained polyhydroxyalkanoate was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-GEL Super HM-H, solvent: chloroform, converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 41,500$ and a weight-averaged molecular weight $M_w = 93,400$.

[0741]

1.00 g of the obtained polyhydroxyalkanoate copolymer, represented by the chemical formula (181), was dissolved in 100 ml of a dioxane-ethanol mixed solvent (75 : 25), then 0.22 g of a 5% palladium/carbon catalyst were added, and the reaction system was saturated with hydrogen and agitated for 1 day at the room temperature. After the reaction, the catalyst was removed by a filtration with a membrane filter of 0.25 μm , thereby recovering the reaction solution. The solution was concentrated, then dissolved in chloroform, and re-precipitated from methanol of a 10-times amount. The obtained polymer was recovered and dried under a reduced pressure to obtain 0.66 g of a polymer. An NMR analysis conducted under conditions same as in Example 6 for specifying the structure of the obtained compound confirmed a polyhydroxyalkanoate copolymer containing units represented by a chemical formula (182) as monomer units. Also a proportion of the monomer units was confirmed as unit C by 9 mol% and unit D by 91 mol%.

[0742]

[Chemical Formula 272]



[0743]

Also an average molecular weight of the obtained polyhydroxyalkanoate was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-GEL Super HM-H, solvent: chloroform, converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 35,800$ and a weight-averaged molecular weight $M_w = 81,600$.

10 [0744]

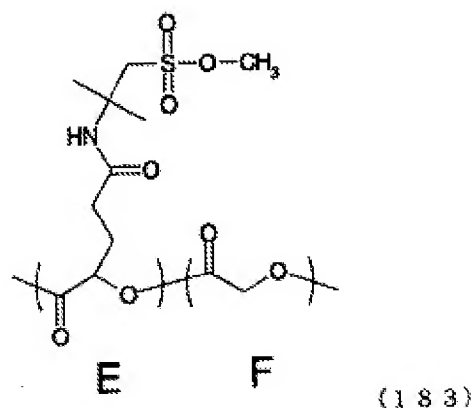
(Example 103)

2.00 g of polyhydroxyalkanoate obtained in Example 100 and constituted of a unit represented by the chemical formula (178) were placed in an eggplant-shaped flask, and dissolved by adding 100 ml of THF. The solution was placed under a nitrogen atmosphere and agitated at -78°C . Then 18.9 ml of a 2M THF solution of lithium diisopropylamide were slowly added and the mixture was agitated for 30 minutes at -78°C . Then 16.68 g of methyl 2-acrylamide-2-methylpropane sulfonate were added and the mixture was agitated for

30 minutes at the room temperature. After the reaction, the reaction mixture was poured into 400 ml of an aqueous solution of ammonium chloride, then 200 ml of dichloromethane were added and the organic layer
5 was separated. The organic layer was recovered after washing three times with 100 ml of water, and the solvent was distilled off to recover a crude polymer. It was then dissolved in 12 ml of THF, and was re-precipitated in methanol of a 50-times amount of that
10 of THF required for dissolving. The precipitate was recovered and dried under a reduced pressure to obtain 1.22 g of polymer. An NMR analysis conducted under conditions same as in Example 6 for specifying the structure of the obtained polymer confirmed a
15 polyhydroxyalkanoate containing units represented by a chemical formula (181) as monomer units. It was also confirmed that a proportion of the monomer units was unit A by 6 mol% and unit B by 94 mol%.

[0745]

20 [Chemical Formula 273]



[0746]

An average molecular weight of the obtained polyhydroxyalkanoate was evaluated by gel permeation chromatography (GPC: Tosoh HLC-8220, column: Tosoh TSK-GEL Super HM-H, solvent: chloroform, converted as polystyrene). As a result, there were obtained a number-averaged molecular weight $M_n = 37,400$ and a weight-averaged molecular weight $M_w = 78,500$.

10 [Industrial Applicability]

[0747]

The present invention provides a novel polyhydroxyalkanoate containing, in a side chain, a vinyl group or a carboxyl group as a reactive group in the molecule, a novel polyhydroxyalkanoate containing a unit having an amide group and a sulfonic acid group in the molecule, and a producing method therefor. The novel polyhydroxyalkanoate having a vinyl group or a carboxyl group is capable of introducing a functional group utilizing such reactive group and is therefore

20

applicable to a functional material. Also the
polyhydroxyalkanoate containing a carboxyl group or a
unit having an amide group and a sulfonic acid group
has an excellent melt working property and an
5 adaptability to organisms, is thus anticipated for soft
members for medical use.

[Name of the Document] Abstract

[Abstract]

[Problem(s)] The invention is to provide a novel
polyhydroxyalkanoate having a reactive functional group
5 within a molecule, a novel polyhydroxyalkanoate having
a novel function by a chemical modification of the
polyhydroxyalkanoate having the reactive functional
group, and a producing method therefor.

[Means for Solving the Problem(s)] A vinyl group of a
10 polyhydroxyalkanoate containing a unit having the vinyl
group in a side chain is utilized for deriving a
polyhydroxyalkanoate containing a unit having a
carboxyl group or an amide group and a sulfonic acid
group in the molecule.

15 [Elected Drawing] None